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JOURNAL OF SCIENCE.

CONDUCTED BY

SIR WILLIAM THOMSON, KNT. LL.D. P.R.S. &c.

GEORGE FRANCIS FITZGERALD, M.A. F.R.S.

AND

WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——"Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

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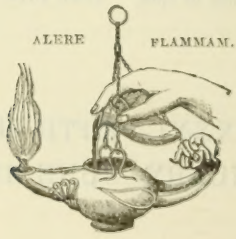

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THE

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PHILOSOPHICAL MAGAZINE

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[FIFTH SERIES.]

JANUARY 1891.

I. *The Refraction and Dispersion of Fluorbenzene and allied Compounds.* By J. H. GLADSTONE, *Ph.D.*, *F.R.S.*, and GEORGE GLADSTONE*.

DR. SIDNEY YOUNG recently had the kindness to place at our disposal an interesting series of compounds for optical examination. They were the halogen substitution-compounds of benzene described by him (Journ. Chem. Soc. 1889); substances that had been prepared with great care, and which were redistilled before they were handed to us.

The following were the determinations of the principal lines of the solar spectrum :—

	Temp. C.	Density.	Refractive Index.					
			A.	C.	D.	F.	G.	H.
Fluorbenzene ...	22·8°	1·0207	1·4563	1·4606	1·4646	1·4751	1·4849	1·4933
Chlorobenzene ...	22·5	1·1047	1·5135	1·5184	1·5232	1·5351	1·5469	1·5573
Bromobenzene ...	23·5	1·4928	1·5469	1·5505	1·5577	1·5715	1·5846	1·5962
Iodobenzene	22·2	1·8300	1·6054	1·6124	1·6197	1·6374	1·6537	1·6699

* Communicated by the Authors. The greater part of this paper was communicated to the British Association, September 1890.

These figures give the following molecular refraction, *i. e.* the refractive index minus unity, divided by the density and multiplied by the atomic weight, $\left(\frac{\mu-1}{d}\mathrm{P}\right)$, which is usually indicated now by R:—

	Formula.	R_A.	R_C.	R_D.	R_F.	R_G.	R_H.
Fluorbenzene ...	C_6H_5F	42·92	43·33	43·70	44·68	45·61	46·40
Chlorobenzene ...	C_6H_5Cl	52·29	52·79	53·28	54·52	55·69	56·75
Bromobenzene ...	C_6H_5Br	57·52	57·90	58·65	60·11	61·48	62·69
Iodobenzene	C_6H_5I	67·49	68·27	69·08	71·05	72·87	74·68

Before dealing with these observations, it may be well to compare them with figures obtained from totally different specimens of bromobenzene and iodobenzene, which have not yet been published. The observations on bromobenzene were part of a series made some years ago with a view of testing the law that the specific refractive energy of a liquid is very little, if at all, altered by changes of temperature. The method adopted was that of determining the refractive index and density of the same specimen on a cold winter's day and on summer days, the liquid being carefully preserved in a well-stoppered bottle between the observations. The iodobenzene was a specimen prepared by Dr. Perkin.

	Temp. C.	Density.	μ_A.	μ_D.	μ_F.	μ_H.
Bromobenzene ...	1°·5	1·51905	1·5581	.....	.....	1·6080
,, ...	23·3	1·49225	1·5476	1·5586	.....	1·5971
,, ...	30·0	1·4833	1·5442	.....	.....	1·5926
Iodobenzene	7·0	1·8537	1·6129	1·6275	1·6450	1·6777

These, reduced to the molecular refraction, are as follows :—

	Temp. C.	R_A.	R_D.	R_F.	R_H.
Bromobenzene	1·5°	57·68	.....	.....	62·83
„	23·3	57·62	58·76	.....	62·81
„	30·0	57·60	.....	.....	62·72
Iodobenzene	7·0	67·45	69·06	70·98	74·58

These figures are almost identical with those determined from Dr. Young's specimens. They not only increase our confidence in the accuracy of the data, but the experiment with bromobenzene shows that we may practically disregard the question of temperature.

Adopting the data in the first two tables, we can estimate the molecular refraction of each halogen in combination by deducting the value for C_6H_5. This has been arrived at by taking the average refraction of several good specimens of benzene for the six lines, and by subtracting from them the assumed value for hydrogen.

	R_A.	R_C.	R_D.	R_F.	R_G.	R_H.
C_6H_6	43·59	44·01	44·48	45·52	46·50	47·39
H	1·30	1·31	1·31	1·32	1·33	1·34
C_6H_5	42·29	42·70	43·17	44·20	45·17	46·05

Deducting these figures from the values given in the second Table, we obtain those of fluorine, chlorine, bromine, and iodine for the several lines:—

	R_A.	R_C.	R_D.	R_F.	R_G.	R_H.
Fluorine	0·63	0·63	0·53	0·48	0·44	0·35
Chlorine	10·00	10·09	10·11	10·32	10·52	10·70
Bromine	15·23	15·20	15·48	15·91	16·31	16·64
Iodine	25·20	25·57	25·91	26·85	27·70	28·63

So far as the well-known halogens chlorine, bromine, and iodine are concerned, these figures are principally interesting as compared with the values already determined for them in other organic compounds. From their combinations with the compound radicals (C_nH_{2n+1}), the numbers given in the first division of the following table have been deduced; but from some other organic compounds, such as chloroform and its congeners, olefine compounds, &c., somewhat higher numbers have been obtained, as in the second division of the table*. The third division gives the figures obtained from the benzene compounds. In each case merely the molecular refraction for the line A is given, with the molecular dispersion, that is, the difference between R_H and R_A.

	Compound radicals.		Olefine compounds.		Benzene substitution compounds.	
	R_A.	$R_H - R_A$.	R_A.	$R - R_A$.	R_A.	$R_H - R_A$.
Chlorine	9·9	0·45	10·0	0·50	10·0	0·70
Bromine	15·3	1·03	15·2	1·22	15·2	1·41
Iodine	24·5	2·60	25·4	3·65	25·2	3·43

It is evident that the values of these ordinary halogens in the benzene substitution-products are analogous to their values in the olefine compounds rather than the others. This is more significant in the dispersion than in the refraction.

But a greater interest attaches to the optical properties of fluorine. No organic compound containing this element had hitherto been examined, while it was known that the refraction of fluorine in its mineral compounds is extremely small. A glance at the sixth Table will show that in the benzene compounds also the effect of fluorine upon the light transmitted is very little. But there is another peculiarity. Whereas the values of chlorine, bromine, and iodine increase from A to H, those of fluorine regularly decrease; so that, in fact, while the refraction-equivalent for A is only 0·63, the dispersion for H—A is actually a negative quantity, —0·28.

Lest this anomalous result might be due to our having

* This distinction is only partially recognized in the paper on "Dispersion Equivalents" in Proc. Roy. Soc. xlii. (1887).

employed the old formula $\frac{\mu-1}{d}P$, we have calculated it also according to Lorenz's formula $\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{P}{d}$; this gives the atomic refraction of fluorine at 0·92 for the line A, and 0·84 for the line H, showing again a minus dispersion.

No minus dispersion-equivalent of the kind has hitherto been met with, unless it be in some of the thin metallic prisms examined by Kundt, and more recently by du Bois and Rubens. It is true that in iodine vapour, as in fuchsin and a few other substances, the irrationality of the spectrum is so great that the order of certain parts is actually reversed, but there is not the regular progressive reversion exhibited in the case of fluorine.

The refraction-equivalent of fluorine had been already determined by Mr. George Gladstone at from 0·29 to 0·32 from observations on metallic fluorides, and at from 0·59 to 0·84 from observations on fluosilicates. It became of interest to see whether the same fluorides would indicate this reversed dispersion.

Fluor-spar.—Among the many determinations that have been made of the refraction of fluor-spar there are three which will answer our purpose, as they give the index of several lines. Not one of them gives the density of the particular specimen; but we shall not be far wrong in taking 3·18 as the specific gravity.

Baille (*Annales du Conservatoire*, vii. 1867) gives the refractive indices for the lithium-line, C, D, F, and a blue copper-line. From these we may calculate the molecular refraction; and from the number so obtained, by subtracting the values for calcium, we get the presumed values for two atoms of fluorine for different parts of the spectrum.

	Lithium red.	C.	D.	F.	Copper blue.
CaF_2	10·61	10·61	10·63	10·70	10·77
Ca	10·07	10·08	10·15	10·33	10·51
F_2	·54	·53	·48	·37	·26

From the figures given by Stefan (*Wiener Ber.* lxiii. 1871) the following may be deduced :—

	B.	D.	F.	G.	H.
CaF_2	10·60	10·64	10·72	10·79	10·84
Ca	10·05	10·15	10·33	10·52	10·65
F_2	·55	·49	·39	·27	·19

Sarasin (*Ar. Genève*, x. 1883) gives the refractive indices of fluor-spar from the line A to very far into the ultra-violet. In the figures so given there seems to be no break, but a regular progression quite comparable with that of quartz. It is only possible for us to calculate the amount due to fluorine up to the line H.

	R_A.	R_a.	R_B.	R_C.	R_D.	R_F.	R_h.	R_H.
CaF_2	10·57	10·59	10·60	10·61	10·64	10·72	10·82	10·84
Ca	10·00	10·03	10·05	10·08	10·15	10·33	10·57	10·65
F_2	·57	·56	·55	·53	·49	·39	·25	·19

All these different calculations from the indices given by different observers show not only the small atomic refraction for fluorine, but also a regular decrease on proceeding from the less refrangible to the more refrangible portion of the spectrum.

Potassium Fluoride.—We have made two observations on aqueous solutions of potassium fluoride. They were separate preparations of the salt.

	Per cent.	Temp.	d.	μ_A.	μ_H.
Potassium fluoride	39·64	25	1·413	1·3793	1·3741
,, ,, ...	34·24	13·5	1·3306	1·3541	1·3692

These give the following molecular refractions, from the mean of which we have deducted the value for potassium :—

	Per cent.	R_A.	R_H.
Potassium fluoride	39·64	8·15	8·38
„ „	34·24	8·42	8·70
Mean value ... KF		8·28	8·54
K		7·85	8·36
F		0·43	0·18

Ammonium Fluoride.—The salt was prepared by saturating ammonia with hydrofluoric acid and gently evaporating down *in vacuo*. An aqueous solution containing 36·88 per cent., having a specific gravity of 1·1734 at 10°·7 C., gave indices for A = 1·3689, for F = 1·3782, and for H = 1·3853. The molecular refractions calculated from these are given below, and the value of NH_4 is deducted :—

	R_A.	R^F.	R_H.
NH_4F	10·69	10·97	11·16
NH_4	10·26	10·55	10·81
F	0·43	0·42	0·35

Hydrofluoric Acid.—Notwithstanding the difficulty of working with hydrofluoric acid, we succeeded in obtaining a determination for the line D in an aqueous solution of this substance. The strength was 23·2 per cent.; the specific gravity was 1·101 ; the refractive index was 1·3155 ; the molecular refraction for D was therefore 2·64. Deducting 1·31 for the hydrogen, we obtain $R_D = 1·33$ for the fluorine. This is a somewhat larger figure than what is given by other compounds ; but that is only in accordance with what occurs in the case of the other halogen acids, which always give figures in excess of theory. The length of the spectrum was evidently very small, but no trustworthy measurements were made.

Hydrofluosilicic Acid.—Different preparations of this acid in aqueous solution gave rather discordant results. But the two most trustworthy gave the following :—

	Per cent.	Temp. C.	Density.	μ_A.	μ_F.	μ_H.
Hydrofluosilicic acid...	36·72	14°3	1·3918	1·3431	1·3507	1·3568
,, ,, ...	22·80	11·0	1·2198	1·3390	1·3472	1·3536

The next table gives the molecular refraction calculated from these two sets of observations; and from the mean value is deducted the usual values for hydrogen, and the following values for silicon, viz. $R_A = 7{\cdot}07$, $R_F = 7{\cdot}26$, and $R_H = 7{\cdot}39$.

		Per cent.	R_A.	R_F.	R_H.
Hydrofluosilicic acid ...		36·72	15·02	15·13	15·21
,, ,, ...		22·80	15·05	15·32	15·47
Mean value	H_2SiF_6		15·03	15·22	15·34
	H_2Si		9·67	9·90	10·07
	F_6		5·36	5·32	5·27

which gives the R_A for fluorine $= 0{\cdot}89$, and a scarcely perceptible negative dispersion. It is of course quite possible that in the case of this acid also the refraction may be raised above the normal.

Solid Fluosilicates.—Messrs. Topsoe and Christiansen have determined the refraction of a number of crystalline fluosilicates for the lines C, D, and F. Unfortunately only one of these belongs to the regular system of crystals, viz. the fluosilicate of ammonium. The refraction-equivalents for this one are given below, and from these are deducted the values for silicon and ammonium.

	R_C.	R_D.	R_F.
$(NH_4)_2SiF_6$	33·14	33·26	33·50
$(NH_4)_2Si$	27·78	27·93	28·36
F_6	5·26	5·33	5·14

This gives R_C for fluorine = 0·88, and, again, a scarcely appreciable negative dispersion.

As the six metallic fluosilicates are all doubly refractive, and we do not know how to deal with that phenomenon, we have not endeavoured to make any precise calculation, especially as the dispersion of the metallic element in each case has not yet been determined. Mr. George Gladstone has already shown that they give a probable refraction-equivalent for fluorine varying from 0·62 to 0·84; and it is quite evident that the dispersion is excessively small, even if it be not a negative quantity.

These results all tell the same tale as fluorbenzene in regard to the optical properties of fluorine. It is true the figures do not appear very accordant; but it must be remembered that all the errors of experiment as well as those arising from impurity of substance fall upon these residual numbers, and where the numbers are so very small discrepancies appear important which would otherwise scarcely be noticed. The values taken for the atomic refraction and dispersion of silicon and the metals must be looked upon as merely approximate; but, whatever rectifications may be made in them hereafter, it is hardly possible that they should affect our general conclusions, viz. that the atomic refraction of fluorine in combination is extremely small, in fact less than 1·0, and that it is smaller for the violet than for the red end of the spectrum.

II. *The Chemical Equilibrium of Solids, in its Relation to Pressure and to Temperature.* *By* Carl Barus*.

1. In a recent number of the 'American Journal,'† I communicated certain data on the effect of dilatational strain on the electric resistance of glass. These experiments, though decisive as to results, were somewhat complex in character; and from their important bearing on the chemical equilibrium of solids, I resolved to attack the subject from a new point of view. The present work is direct, and I hoped that results could thus be reached without necessitating auxiliary hypotheses or experiments. In this expectation I deceived myself: the insulating oil, which transmits pressure to glass, shows a pressure-coefficient usually much larger than the glass itself. Both must therefore be studied. Nevertheless, the confirmation of my earlier results which the present

* Communicated by the Author.

† Amer. Journ. xxxvii. pp. 339 to 351 (1889).

paper gives, is gratifying. I am thus able to carry the deductions one step further. Again, the behaviour of liquid hydrocarbon insulators under pressure presents many points of special interest in relation to the formation and occurrence of ions.

As a result of the investigation of different oils, I have been able to increase the efficiency of my screw-compressor * in marked degree. By using a sticky *mineral* machine-oil, thick enough to be almost opaquely fluorescent †, not only does the screw of my apparatus run more easily, but leaks at high pressure are practically absent. Moreover, the gasket of marine glue is not in any measure dissolved (this is the case with sperm-oil), and it therefore lasts indefinitely. Finally, the insulation of barrel and piezometer is now at least as high as 10,000 megohms, and need not be less than 1000 megohms. This is an important requisite in experiments like the present.

The special work on the effect of pressure on the electromotive force of the cell NaHg glass/Hg has intrinsic interest apart from its subsidiary purpose as embodied in the present text. From experiments to be published in a Bulletin of the U.S. Geological Survey, I infer that the secret of the relation of the Peltier contact to the Volta contact will probably manifest itself, if a suitable cell, suitably compressed, be carried through a large range of temperature, quite into red heat.

I gain another inference by comparing the present results with the data of my last paper ‡, on the effect of pressure on the thermal relations of metallic and electrolytic conductivity.

Finally, the present work is tributary to an extended series of experiments on the relation of melting-point and pressure, as will appear in § 6. Thus it forms an essential part of the work suggested by Mr. Clarence King.

Apparatus.

2. Hydrostatic pressures as high as 1500 atmospheres were applied. Having found that within the limits of the present paper nothing essentially novel was gained by excessively high values of pressure, I facilitated my work by avoiding them as much as possible.

3. To obtain different constant temperatures, the tubes were exposed successively to vapours issuing from water (100°), turpentine (160°), naphthalene (215°), and diphenylamine (310°). A serviceable continuous vapour-bath for this purpose

* Phil. Mag. (5) xxx. p. 338 (1890).

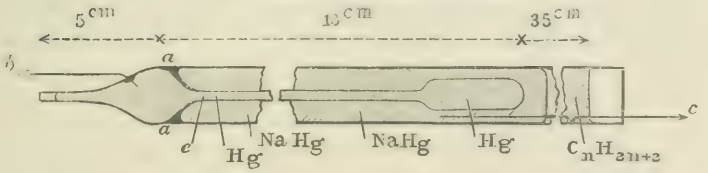
† Possibly containing rubber.

‡ Amer. Journ. xl. pp. 219–222 (1890).

is also described in the paper last cited. I need only add that the ends of the brazed copper bath are provided with screw stuffing-boxes of the ordinary kind, in which either asbestos packing or a hollow cylinder of cork may be forced home by the gland. Vapour-baths must be removed hot. They then slide off the smooth steel piezometer easily, and without jarring the tube.

4. In the compressor, the arrangement adopted is that of insulating the piezometer-tube from the barrel- and compression-appurtenances. Inasmuch as in some of the experiments the resistances to be measured amount to several hundred megohms, the piezometer-insulation must be perfect to at least several thousand megohms. How this was gradually accomplished will be explained in §§ 10 *et seq.* Gutta-percha-covered wire and raised hard-rubber commutators are essential. Care must be taken to insulate the water-jackets which cool the ends of the piezometer, and to allow the efflux water to drop into a cistern discontinuously. The burners which heat the vapour-bath must be insulated to prevent conduction through the flame, &c. At high temperatures, where the resistance of the glass will have decreased several hundred to one, many of these precautions are superfluous. They are always necessary when oils are examined.

Fig. 1.—Tube for measuring the Pressure-increments of the Electric Resistance of Glass.



5. The original apparatus for measuring the resistance of compressed glass is shown in figures 1 and 2, of which the latter is a diagram. Fig. 1 consists essentially of two coaxial glass tubes, the larger completely surrounding the smaller. The diameter of the larger (thick-walled) tube is ·4 to ·5 centim. ; that of the inner (thin-walled) tube is ·2 centim. They are joined along the ring *a a*. Two separate compartments are thus formed, the inner of which is filled with pure mercury, and the outer with sodium amalgam, to a sufficient length to completely envelop the inner tube. The end of the large tube contains hydrocarbon oil, both to protect the amalgam against moisture or air, when the tube is not in place,

and also to prevent the saponification of sperm-oil and to eliminate condensable air, when the tube is in place. Mercury and the fluid amalgam are to be introduced by aid of the air-pump, care being taken to boil out all traces of air. The mercury of the inner compartment is in galvanic connexion with the platinum wire *b*, which in its turn connects with the piezometer-tube. Hence *b* need not be insulated. The amalgam is pierced by the terminal *c*, completely insulated from the piezometer by the *unbroken length of cold glass tube* surrounding the wire. To prevent the wire from being pulled out of place during the adjustments, *c* is sealed in the inside of the insulator-tube as shown in the figure. This terminal is in galvanic connexion with the barrel. It is seen that the tube is virtually a galvanic cell, NaHg/glass/Hg, and is reversible.

Under the influence of hydrostatic pressure, the figure of the glass tube is symmetrically reduced in size. Hence, with regard to the conduction taking place across the walls of the *inner* tube, the resistance would be increased, in consequence of changes of dimensions, only by the amount in which the length of the inner tube is diminished. In other words, if $r=sl/2\pi RL$, where s, l, R, L denote respectively specific resistance, thickness, radius, and length of the thin tube, then the dimensional effect of pressure is $\delta r=(sl/2\pi RL)\times\delta L/L$, nearly. But all such values ($\delta L/L$ being less than ·1 per cent. per 1000 atm.) are negligible in comparison with the relatively large pressure-coefficients actually obtained (*cf.* Tables I. to VIII.), and to be interpreted with reference to $s'-s$.

Fig. 2.—Diagram of Tube in place.

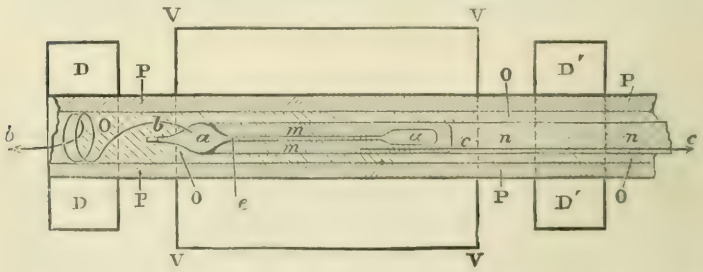
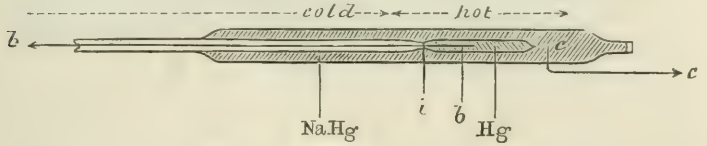


Fig. 2 (diagram) shows the resistance-tube in place. PP is the tubular steel piezometer, surrounded by the vapour-bath V V, and the cold-water jackets D D and D′ D′, and filled with the oil, O O, by which the pressure is transmitted. The inner compartment of the glass tube is at *a a* (mercury),

the outer compartment at *m m* (sodium amalgam), with petroleum at *n n*. The terminal wires are shown at *b b* (cathode connecting with the piezometer) and at *c c* (anode, insulated).

6 *a*. In the course of my work, however, I found it essential to connect *c c* with the piezometer and to insulate *b b*; for by thus reversing the tube there is no tendency of short-circuiting through oil and the *outer* tube. Indeed, so important is this adjustment that I further modified the tube, fig. 1, in the way indicated in fig. 3.

Fig. 3.—Improved Form of the Tube.

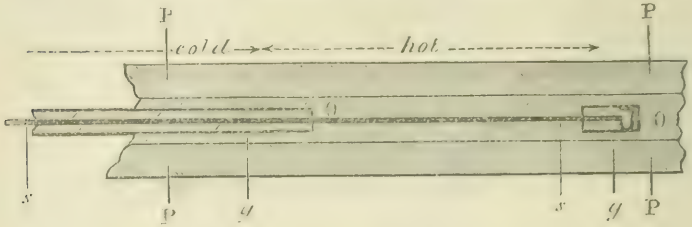


Here the inner compartment is filled with mercury to only about 7 centim. of the end. The remainder of the tube, containing hydrocarbon oil, runs completely through the piezometer into the barrel, with which the insulated platinum terminal connects. To keep the mercury in place, the inner tube is drawn down to a smaller diameter (see *i*, fig. 3), into which the mercury meniscus projects. Air is excluded by boiling the mercury with the platinum wire in place. The latter amalgamates externally, but careful handling is none the less advisable. The outer tube, with its filling of sodium amalgam, not only envelops the inner mercury-thread, but extends in both directions as far as the *cold* parts of the surrounding piezometer-tube. Since *c c* connects with this, no current will pass through the film of *hot* oil and the outer glass tube. All currents between piezometer and barrel must therefore pass through the walls of the inner glass tube—a condition which is further insured by making NaHg|glass|Hg the acting electromotive force. I have purposely described these precautions at length; and their importance is obvious when it is remembered that the oil medium has a larger pressure-coefficient than glass, and that the insulation of oil sometimes breaks down in marked degree with rise of temperature (§ 19). The effect of cold oil can be found preliminarily, when the whole apparatus is cold.

6 *b*. I have finally to show the apparatus for testing the resistance and pressure-coefficient of the liquid insulators at different temperatures. This is given in fig. 4 (diagram), and consists essentially of a cylindrical steel rod *s s*, adjusted

coaxially with the steel piezometer P P, containing the oil to be tested. Tubes of glass, *g g*, hold the rod *s s* in position. Owing to the fact that above 200° glass conducts better than most hydrocarbon oils, this insulating arrangement is not quite

Fig. 4.—Arrangement for measuring the Pressure Increments of the Electric Resistance of Liquid Insulators.



satisfactory ; but by using thin-walled glass tubes filled with the oil, the data so obtained are sufficient for the purposes of the present text, since the rate of breakdown with temperature is accentuated. It is seen that the measuring-current passes from the piezometer P P, through the cylindrical layer of oil, into the rod *s s*, and thence to the battery. The diameters of steel core and piezometer-tube being ·13 and ·63 centim. respectively, and the exposed part 9 centim. long, the specific resistance of the layer of oil is easily computed (§ 19).

6 *c*. *Digression.*—By filling the greater part of the closed end of the inner tube (fig. 1 or 2) with the substance to be examined, and the open end as far as *e* with mercury, the tube is available for the study of melting-point and pressure. In such a case the forward motion of the inner mercury meniscus due to pressure proportionately decreases the resistance of the arrangement by increasing the opposed surfaces of mercury and sodium amalgam. Increased delicacy is secured by enlarging the bulb at the end of the inner tube. At the solidifying-point the sample usually undergoes a phenomenal reduction of volume, corresponding, therefore, to a similarly large reduction of resistance. This occurrence I propose to use as the criterion of solidifying-point and of melting-point. The apparatus is available above 100° under any pressure up to several thousand atmospheres.

The criterion specified is also available when a fine platinum wire is stretched through contiguous coaxial columns of the substance and of mercury in a vertical piezometer.

7. Resistances were first measured by a bridge method ; but owing to the fact that electromotive forces are involved which may themselves vary with pressure, I lost faith in the

safety of these methods and replaced them by simple circuit methods. The errors to be guarded against are primarily in the experiment itself. Again, the resistance-tube (figs. 1–3) is well adapted for simple circuit-work, since the electromotive force NaHg/glass/Hg may exceed a volt, and the only pronounced resistance is in the cell. Only at 100° need auxiliary cells be inserted.

Throughout the work the low-pressure or fiducial resistance is measured *before* and *after* the high-pressure resistance. This safeguard is necessary. From three to five minutes were allowed for the elimination of thermal discrepancies. The fiducial resistance is to be measured under a pressure of 100 to 200 atmospheres, both to condense the air retained in the pump and to make the oil less compressible (§ 32). Not much care was taken in measuring the absolute resistances, since the inferences of this paper are to be drawn from the increments.

8. In the high-resistance experiments I used the Elliott square pattern of Thomson's high-resistance astatic galvanometer. The readings, however, were made by Poggendorff's method of telescope and scale. To adapt Thomson's concave-mirror adjustment for this purpose, I compensated the curvature by an ordinary "No. 36" concave spectacle-glass fixed in front of the mirror, diffuse light being suitably screened off. Glass "No. 36" slightly under-compensates the mirror, leaving some magnification which is not undesirable. In how far a weak telescope may be made to do the service of a more powerful instrument, in virtue of the concave mirror and a lens even weaker than No. 36, remains to be seen. With the above adjustment of lens and mirror, using a telescope magnifying somewhat over 20 diameters, and a scale somewhat further than 2 metres from the mirror, I obtained an image about 4·5 centim. long and sufficiently distinct for all practical purposes. Thus, if one volt act in one million megohms, the current produced would only just escape detection.

At 200° the galvanometer was suitably shunted.

9. Regarding other manipulations, the paper cited in § 2 will have to be consulted. Electromotive forces were measured by a zero method.

Observations.

10. Table I. contains data for the apparent change of the resistance of glass with pressure, when the liquid which transmits pressure is ordinary saponifiable sperm-oil. Here θ denotes the temperature of the vapour-bath, approximately,

and R the resistance of the uncompressed glass shell. $\delta R/R$ is the *increment* of resistance, R, corresponding to the pressure-increment δp, where the initial pressure is at least 50 atmospheres (§ 7). $k_r = \delta R/R.\delta p$ is the pressure-coefficient. To save space, I have taken the mean of the two or three complete triplet observations for each δp given. The Table contains six independent series of experiments, made at different times and often with different tubes. The adjustment, however, was in the main that of fig. 2, reversed.

TABLE I.—Apparent Effect of Pressure (in atmospheres) on the Resistance of Glass, in an insulating medium of Animal Sperm-Oil.

Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$10^6 \times k_r$.	Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$10^6 \times k_r$.
I. 215°. $117 \times 10^3\omega$. 182.	82 160 213	470 835 1180	174 193 181	III. 310°. — 116.	51 99 165	480 877 1320	110 113 125
I. 215°. $117 \times 10^3\omega$. 182.	75 157 217	455 825 1160	167 191 188	IV. 100°. — 360.	164 330	450 930	365 355
I. 310°. $6 \times 10^3\omega$. 137.	59 117 170	497 830 1175	119 142 145	IV. 160°. — 200.	112 102 111	515 525 610	217 196 185
I. 310°. $6 \times 10^3\omega$. 134.	61 116 158	470 845 1155	130 136 137	VI. 100°. — 660.	420 420	605 650	685 640
II. 215°. $122 \times 10^3\omega$. 178.	67 135 195	390 750 1070	171 180 182	VI. 160°. — 203.	127 136 141	655 644 674	194 211 209
II. 310°. $9 \times 10^3\omega$. 121.	49 97 145	450 790 1120	112 122 127	VI. 215°. 184.	126 123 127	657 691 688	192 177 184
III. 215°. $130 \times 10^3\omega$. 161.	85 165 219	516 1000 1405	163 163 156	VI. 310°. $10^3\omega$. 140.	97 89	689 639	143 138

11. A graphic construction shows the character of these divers series to be identical, though the individual pressure-coefficients show marked variation. The data of the third series are made in connexion with the following data of Table II., in which electromotive forces are measured before and after the resistance measurements. As a rule, the galvanometer-needle does not reach its position of equilibrium at once; the slow changes registered are probably due to gradually vanishing thermal discrepancies (§ 37).

12. Table II. gives results for the effect of pressure on the electromotive force NaHg/glass/Hg. Here θ is the temperature of the vapour-bath, and e the observed electromotive force, in volts, corresponding to the pressure δp, when the initial pressure is above 50 atmospheres (§ 10). $k_e = \delta e/e \,.\, \delta p$ is the pressure-coefficient. Five minutes were allowed per observation. Special experiments showed that e decreases on cooling. The medium for transmitting pressure is again ordinary animal sperm-oil. Earlier observations were discarded, and results are condensed as far as possible.

TABLE II.—Apparent Effect of Pressure on the Electromotive Force of NaHg/glass/Hg.

θ. Mean $k_e \times 10^6$	δp.	$e \times 10^4$.	$10^3 \times k_e$.	θ. Mean $k_e \times 10^6$.	δp.	$e \times 10^4$.	$10^6 \times k_e$.
100°.	0	5180	—	†215°.	0	11182	—
230.	720	5950	210	10·9.	488	11244	11·3
	0	4300	—		0	11210	—
	1080	5440	245		992	11332	11·0
					0	11224	—
*215°.	0	10872	—		1378	11374	9·7
7·3.	533	10904	5·5		0	11214	—
	0	10912	—		550	11286	11·7
	524	10950	6·7				
	0	10922	—	310°.	0	10658	—
	551	10968	7·7	5·1.	505	10672	2·5
	1010	10996	6·8		0	10666	—
	0	10924	—		480	10706	7·8
	535	10976	8·9				
	1011	11008	7·7				
	0	10924	—				
	542	10972	8·2				
	1033	11004	7·2				
	1441	11024	6·5				
	0	10912	—				
	540	10968	9·6				
	1027	11004	8·3				
	1436	11028	7·4				

* Before the resistance-measurements.
† After „ „ „

13. To facilitate measurement, the greater number of experiments are made at 215°. Polarization was observed; and for this reason the measurement of temperature-coefficients by removing and readjusting vapour-baths was not tried. The increment of electromotive force is largest immediately after compression (temporary effect), and then decreases to the apparently constant values of the Table. The converse holds for the decrement on removing pressure. At 100° no satisfactory results could be obtained (§ 34). At 310°, although the temporary effects were distinct, the permanent effects are not warranted.

14. Table III. contains results, given on a plan identical with that of Table I., for the case in which the glass tube (fig. 1) was removed and the steel rod (fig. 4) inserted. In this way the pressure-coefficient of ordinary sperm-oil was found. Table III. also contains results for glass made after the work with oil.

TABLE III.—The Insulation and Pressure-Coefficient of Sperm-Oil. $p_0 = 100$ atm. Pressure-coefficient of glass.

Series No. θ. R. Mean $10^6 \times k_r$.	$10^3 \times$ δR/R.	δp.	$10^6 \times k_r$.	Series No. θ. R. Mean $10^6 \times k_r$.	$10^3 \times$ δR/R.	δp.	$10^6 \times k_r$.
1. 20°. $18 \times 10^6 \omega$. +5700.	3300 3500 8100 6500 2200	540 573 1240 1140 553	6200 6100 6500 5700 4000	Glass tube inserted.			
				VII. 100°. $240 \times 10^6 \omega$. 620.	347 373	570 580	600 640
1. 100°. $2 \times 10^6 \omega$. +880.	500 550 990 460	550 610 1150 550	910 890 860 840	VII. 215°. $500 \times 10^6 \omega$. 171.	90 94 186	570 560 1000	157 170 186
1. 215°. $300 \times 10^6 \omega$. +330.	180 200 230	550 600 675	330 330 340				

The pressure-coefficient of sperm-oil is therefore decidedly larger, and the specific resistance of this oil is usually smaller, than that of glass (*cf.* § 19, Tables IX. & X.); but the breakdown of resistance with rise of temperature is more marked in the latter case. Nevertheless the data of Table III. cast grave doubt on the trustworthiness of the data of Table I.; and hence a search must be made for more highly insulating

liquids. For obvious reasons I selected the hydrocarbon oils of the paraffin series.

15. Table IV. contains data for the insulation and pressure-coefficient of very volatile gasolene.

TABLE IV.—Behaviour of Gasolene under Pressure. Initial pressure, $p_0 = 200$ atm. Resistance at 20°, $2 \times 10^9 \omega$.

Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$10^6 \times k_r$.	Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$10^6 \times k_r$.
2. 100°. $450 \times 10^6 \omega$ to $130 \times 10^6 \omega$. ± 0.	0	250	0	2. 310°. $220 \times 10^6 \omega$. -1800.	-380 -550 -580 -550 -590	250 300 300 300 300	-1500 -1800 -1900 -1800 -2000
2. 215°. $220 \times 10^6 \omega$ to $150 \times 10^6 \omega$. -890.	-330 -290 -200 -140 -190	250 280 280 220 250	-1300 -1050 -710 -640 -760				

The resistance of gasolene is therefore enormous as compared with sperm-oil, and above 100° more than 100 times that of glass. Moreover the breakdown of the gasolene insulation with temperature is remarkably slow; but owing to the difficulty of keeping the apparatus free from leaks in the case of this very thin oil, I did not make experiments with the glass tube.

A feature of these results is the negative pressure-coefficients found, which themselves decrease algebraically nearly proportionally to the temperature of the oil. At a given temperature the resistance is not constant, but decreases; and since the gasolene is discoloured when removed from the press, the decrease of resistance is undoubtedly a solution-phenomenon. Indeed, I suspect that negative coefficients are possibly to be associated with solution (§ 39).

16. In Table V. data are given for ordinary illuminating oil (petroleum). The glass tube still has the form of fig. 1, reversed. Two sets of experiments were made.

TABLE V.—Insulation and Pressure-Coefficient of Petroleum. Initial pressure, $p_0 = 50$ atm. Pressure-coefficient of glass.

Series No. θ. R. Mean $k_T \times 10^6$.	$10^6 \times$ ∂R R.	∂p.	$10^6 \times k_T$.
3. 20°. $370 \times 10^6 \omega$. +1500.	700 700	460 480	1530 1460
3. 100°. $130 \times 10^6 \omega$. +820.	520 570	580 760	890 750
3. 215°. $40 \times 10^6 \omega$. +274.	134 167 177	570 590 580	234 282 306
3. 310°. $47 \times 10^6 \omega$ to $34 \times 10^6 \omega$. −430.	−285 −281 −229 −223 −192	550 570 570 640 520	−521 −492 −404 −349 −369
Glass tube inserted.			
VIII. 100°. $230 \times 10^6 \omega$. +780.	630 420	570 610	880 680
VIII. 215°. $200 \times 10^6 \omega$. +136.	84 86	630 600	132 142
VIII. 310°. $50 \times 10^6 \omega$. ×43.	20 34 33 40	740 725 665 640	26 34 50 63

Series No. θ. R. Mean $k_T \times 10^6$.	$10^6 \times$ ∂R R.	∂p.	$10^6 \times k_T$.
Petroleum tested again. $p_0 = 200$ atm.			
4. 100°. $740 \times 10^6 \omega$. +1800.	560 750	370 360	1500 2100
4. 215°. $64 \times 10^6 \omega$. +560.	115 193 166 200	310 305 300 300	380 640 553 667
4. 310°. $32 \times 10^6 \omega$. −340.	−115 −175 −100 −105 −140 −115 −130 −105	300 550 285 290 523 298 495 280	−383 −320 −360 −360 −270 −383 −265 −380
Glass tube inserted.			
IX. 100°. $10^6 \omega$. +1330.	400	300	1330
IX. 215°. $700 \times 10^3 \omega$. +93.	20 25 36 30	300 280 300 300	66 88 120 100
IX. 310°. $140 \times 10^3 \omega$. −76.	−25 −32 −17	300 300 300	− 83 −107 − 55

The specific resistance of petroleum is not so high as that of gasolene, though it is more than 20 times that of glass at 215°, and the insulation breaks down less rapidly. The pressure-coefficients decrease in marked degree with rise of temperature, and nearly proportionally to it, and they actually pass from positive to negative values. They are of a larger

order of numerical magnitude than the glass-coefficients. At 310°, where the petroleum-coefficient is negative and the glass-coefficient, according to Tables I. and III., positive, a criterion of the effect of the oil is obtainable. The glass tube ‡ does not stand this test fully, since the pressure-coefficients of oil and glass in series IX. are both negative, though the effect of the glass is a decided algebraic increase of the oil-coefficient. Moreover, as the trustworthiness of a tube like fig. 1 reversed is no longer vouched for, I made the remaining experiments with the tube figure 3. I also tested a better insulating oil.

17. Tables VI. and VII. contain data for the insulation and resistance of thin mineral machine-oil ("mineral sperm"), and also for glass surrounded by it. At 215° the resistance of the liquid is more than 50 times that of glass, and the breakdown in the former case much less rapid. Two glass tubes of the form fig. 3 were used consecutively. In the first of these the internal and external diameters of the inner tube were ·24 and ·34 centim. respectively; in the other the dimensions of the inner tube were those given in § 5.

TABLE VI.—Pressure-Coefficient and Insulation of thin Mineral Machine-oil. $p_0 = 150$ atm. Insulation at 20°, $3 \times 10^9 \omega$.

Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times$ δR R.	δp.	$k_r \times 10^6$.	Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times$ δR/R.	δp.	$k_r \times 10^6$.
5.	400	410	970	5.	95	370	+260
215°.	400	420	960	†310°.	95	340	280
$320 \times 10^6 \omega$.				$50 \times 10^6 \omega$.	140	400	350
+960.				+300.	125	390	320
					400	410	970
5.	−220	410	−525		400	420	960
*215.	−160	430	−370				
$110 \times 10^6 \omega$.	−190	440	−430				
−440.							

* Dirty, after an explosion. † Clean, refilled.

‡ I strongly suspect that some oil had worked itself down into the sodium amalgam, and that this is the true cause of the exceptional behaviour referred to in the text. This inference was sustained by a dissection of the tube after the experiment.

TABLE VII.—Pressure-Coefficient of Glass, surrounded by Mineral Machine-oil. $p_0 = 150$ atm.

Series No. θ. R. Mean $k_T \times 10^6$.	$10^3 \times$ δR/R.	δp.	$k_T \times 10^6$.	Series No. θ. R. Mean $k_T \times 10^6$.	$10^3 \times$ δR/R.	δp.	$k_T \times 10^6$.
XI. 215°. $80 \times 10^3\omega$. +138.	61 59	445 420	137 140	XI. 215°. $190 \times 10^3\omega$. +145.	57 59	400 400	143 147
XI. 215°. $120 \times 10^3\omega$. +143.	53 67	425 420	127 157	XI. 100°. $30 \times 10^3\omega$. +250.	71 94 113	385 365 375	185 260 300
XI. 310°. $6 \times 10^3\omega$ to $8 \times 10^3\omega$. +117.	41 48 46 52 49 48	363 415 420 410 420 415	115 116 112 126 117 115	*XII. 215°. $360 \times 10^3\omega$. +173.	66 69 63	395 395 355	170 175 175
				*XII. 310°. $26 \times 10^3\omega$. +168.	54 60 67	350 350 380	155 170 180

* Another tube of higher resistance.

Repetitions of this work led to virtually the same uniformity of result, as is well evidenced by the close coincidence of the data for 215°. The coefficients of the two tubes, however, are not identical. A feature of Table VI. is the change of sign of the pressure-coefficient, when the oil has become contaminated. It is in these experiments (Table VI.) that I specially observed the apparent accommodation detailed in § 37. As a whole the data are in reasonable conformity with Table I.

18. My final experiments were made with a very sticky *mineral* machine-oil (*cf.* § 1). Two tubes of the form fig. 3, but of different resistances, were used (§ 17).

At 310° the oil-coefficients are negative, whereas the glass-coefficients remain distinctly positive. This seems to be a conclusive test, since an effect of the glass in changing the sign, or in any way increasing the oil-coefficients is inconceivable. The increase of the latter with pressure at 215° (*cf.* Table VIII.) is probably an actual occurrence. The two tubes again differ in their properties.

TABLE VIII.—Pressure-Coefficient and Insulation of sticky Mineral Machine-oil. $p_0 = 150$ atm. Pressure-coefficient of glass. Oil-insulation at 100°, 4×10^9 ω.

Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$k_r \times 10^6$.
6.	530	810	655
215°.	520	820	635
$130 \times 10^6 \omega$.	125	360	350
+510.	155	400	390
6.	−140	440	−320
310°.	−145	410	−355
$18 \times 10^6 \omega$.	−120	420	−285
−296.	−125	450	−280
	−125	470	−265
	−115	430	−270
Tube of low resistance inserted.			
XIII.	52	415	125
100°.	64	420	150
$11 \times 10^6 \omega$.	115	820	140
+135.	99	810	125

Series No. θ. R. Mean $k_r \times 10^6$.	$10^3 \times \delta R/R$.	δp.	$k_r \times 10^6$.
XIII.	73	430	170
*215.	42	450	92
$120 \times 10^3 \omega$.	50	400	125
129.	Tube broken.		
Tube of high resistance inserted.			
XIV.	81	400	202
215°.	84	420	200
$730 \times 10^3 \omega$.	165	830	200
+205.	180	830	220
XIV.	70	415	170
310°.	60	420	145
$36 \times 10^3 \omega$.	130	820	160
+155.	125	780	160
	54	400	135

* Dirty, after an explosion.

19. In Tables IX. and X. I have briefly summarized the statistics of insulation for oil and for glass. All reference is made to 215°, since these measurements are the more reliable. The table is not intended to convey more than a mere estimate of the conditions encountered.

TABLE IX.—Breakdown of Resistance in the case of the divers Oils examined.

	Sperm-oil.	Gasolene.	Petroleum.	Thin mineral machine-oil.	Very thick mineral machine-oil.
Specific resistance at 215°	3×10^6	1800×10^6	400×10^6	1000×10^6	1200×10^6
Relative resistance at 20	60	10	26	300	∞
„ „ 100	7	2	9	30	30
„ „ 215	1	1	1	1	1
„ „ 310	..	1	·6	·5	·1

TABLE X.—Breakdown of Resistance in the case of divers Glass arrangements. Specific resistance at 215°, 19×10^6.

Glass in	Sperm-oil.	Gasolene.	Petroleum.	Thin mineral machine-oil.	Thick mineral machine-oil.
100°	500	...	1400	300	
215	1	...	1	1	1
310	...	...	·2	·2	·05

DEDUCTIONS.

20. It appears from Table I. *et seq.*, that the pressure-coefficient does not decrease with the size of the pressure interval δp. The tendency is rather in favour of an increase, but this is obscure. Hence the results obtained are properties of either the oil or of the glass, and not incidental disturbances. Moreover, I am warranted in taking the means of the divers pressure-coefficients found at any temperature as the probable value at that temperature.

21. Remarks on the discrimination of temporary and permanent effects have been made, §§ 11, 13.

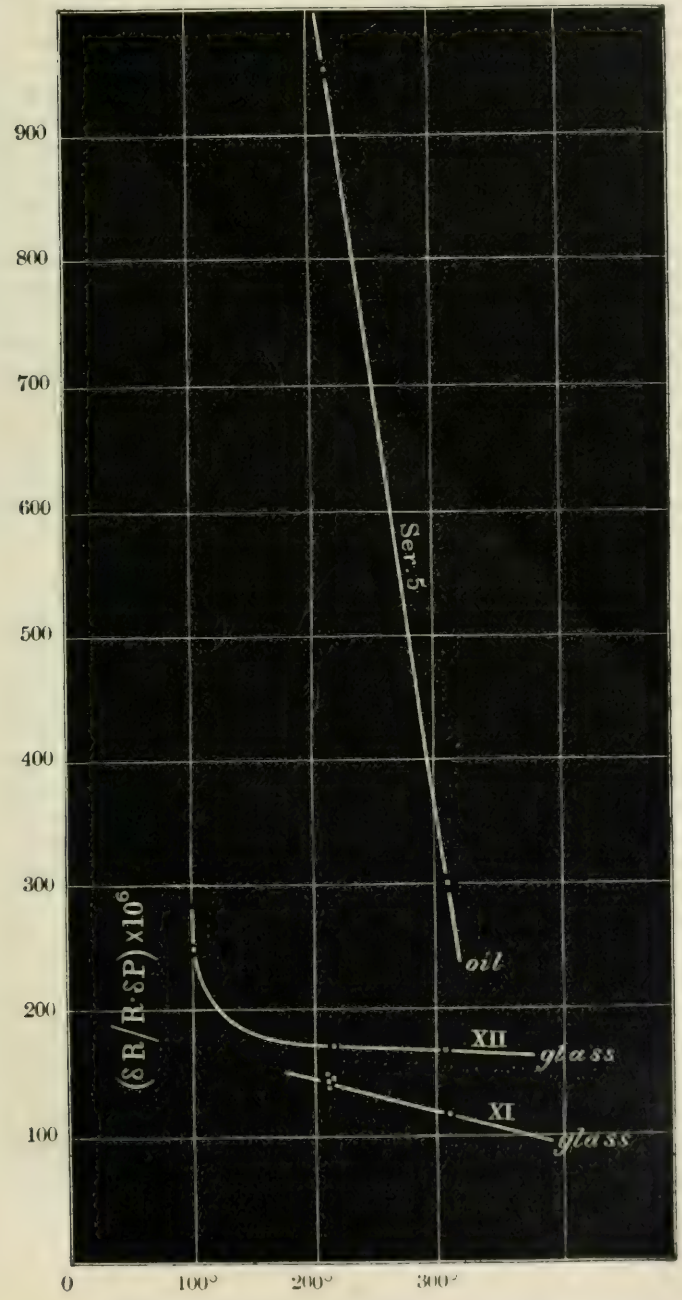
22. In order to obtain a clear insight into the data of Tables I. to VIII., it is best to construct pressure-coefficient as a function of temperature. It would be more in keeping with the present work to coordinate this coefficient with resistance; but the latter data are not sufficiently accurate. In fig. 5 the number of the series is marked on the curve.

23. Turning attention first to the behaviour of the solid insulator, it appears that the electrical resistance of glass increases in very marked degree with the pressure which is brought to bear on it. In my earlier paper*, in which I subjected glass to tensile stress (presumably dilatational), I found that the resistance had pronouncedly decreased. I also found that the results at 360° were not as evident as at 100°. Hence the present and the earlier observations, though attacking the question from opposite points of view, are in accord. I am thus justified in announcing that *the chemical equilibrium of a solid changes with each change of strain* (§ 30).

24. The tables further show that the pressure-coefficient of resistance decreases with rise of temperature; or that the effect of pressure decreases algebraically as the number of free ions available for the transfer of charges becomes greater. In an earlier paper† I showed that the resistance of a liquid

* American Journal, xxxvii. p. 349 (1889).
† American Journal, xl. p. 219 (1890).

Fig. 5.--Charts showing the Relation of Pressure-Coefficient and Temperature for Glass and Hydrocarbon Oil ("mineral sperm").



electrolyte like zinc sulphate in water, or of a liquid metal like mercury, is a decrease of specific resistance. Finally, the present results for insulating-oils contain several examples in which a passage of the positive into the negative pressure-coefficient is directly observed. I conclude that the curve for glass, if prolonged, will eventually intersect the axis of temperature somewhere in the region of low red heat, and that the further course will be negative. Hence for all substances, solid or liquid, there is a point or state of electrolytic dissociation at which the effect of pressure on resistance is *nil*; or at which the increased molecular stability obtained by pushing the molecules nearer together, and, perhaps, of binding the constituents of the individual molecule more firmly together, counterbalances the decrease of the path over which the ion travels in conveying charge. Taking all the results for glass, oils, the solution and the metal into account, it appears that the complete functionality will be given by a curve which is asymptotic both to the vertical in the region of low temperatures and positive pressure-coefficients, and to the horizontal in the region of relatively high temperatures and negative pressure-coefficients. The nature of this curve I have not been able to work out (§ 22), nor will it be the same for all substances.

25. Having thus found a consistent behaviour in metals and electrolytes in relation to strain, I am prepared to accept the proposition italicized in § 23 as true for solids* generally. For the case of metals Osmond † has partially anticipated me, stating that strain more or less completely converts cold metals from one definite molecular condition into another. I have been unable to find, however, that Osmond has any direct evidence to support this assertion, and I have already pointed out ‡ some of the difficulties which Osmond must surmount before his view can gain general credence. If mechanical stress is to convert α-iron into β-iron, it is not to be overlooked that whereas the hardness called temper changes the electrical resistance of steel enormously (as much as 300 to 400 per cent.), the electrical effect of mechanical strain is relatively negligible. Even though much of this discrepancy

* To my knowledge the only experiments on the effect of pressure on the resistance of solid metals are due to Chwolson (Carl's *Repertorium*, xiv. p. 26, 1878), who shows that their pressure-coefficient, like that of mercury, is negative.

† Osmond, *Annales des Mines*, July–August, 1888, p. 6; *Mém. de l'artillerie de la Marine* (Paris, 1888), p. 4. Of course I make no reference against the ingenious experiments from which Osmond infers the spontaneous conversion of α-iron into β-iron at red heat.

‡ 'Nature,' xli. p. 370 (1890).

can be explained away, *direct* experiments on metals confirming Osmond's view will not be easily forthcoming. Two years ago I spent much time in endeavouring to throw light on the polymerization of metals, by studying the hydroelectrics of stretched and soft wires*, by dissolving hard-drawn and annealed iron, by investigating the carburation changes of strained steel; but in no case have I found evidence of an indisputable bearing on the point at issue. Finally, regarding the mere statement † of inferences of the above kind, I believe I anticipated Osmond by interpreting viscosity in solids † with reference to Clausius's theory of electrolysis.

26. The proposition of § 23, taken in connexion with my observation of the occurrence of volume-lag ‡ under isothermal conditions, suggests important inferences on the behaviour of stressed solids generally, and leads naturally to an explanation of hysteresis. If the pressure under which a liquid just solidifies, *cæt. par.*, is in excess of the (positive or negative) external pressure at which it again liquifies (volume-lag §), and if the chemical equilibrium of the solid acted on changes with each change of strain, then, quite apart from considerations *directly* involving the second law of thermodynamics, quite apart from the energy dissipated in the cycle, the solid

* American Chemical Journal, xii. p. 1 (1890).

† American Journal, xxxiii. p. 28, January 1887.

‡ American Journal, xxxviii. p. 408 (1889).

§ A good example of the volume-lag is given by an undercooled liquid like fused thymol (melting at 53°), for instance, which at, say, 30° solidifies under about 500 atm., and does not again liquefy on removing the external pressure. I have worked with para-toluidine, naphthalene, *a*-naphtol, paraffin, and caprinic, palmitic, and monochloracetic acids. My original belief in the general character of these static phenomena has recently been disturbed by new experiments, in which I found for the special case of paraffin that it would be possible to be misled by *local* solidifications of the column under pressure. The volume-lag is always marked when there is even a suggestion of undercooling. The action of pressure is then similar to the closing of a door and opening it again without lifting the latch. Observations made at intervals of 20 minutes each, with palmitic acid, showed that at 66° this substance solidifies between 300 and 400 atm., and then remains solid even between 200 and 300 atm. At 100°, *a*-naphtol solidifies at 500 to 600 atm., and when pressure is being removed it remains solid until about 150 atm. Undercooled caprinic acid at 20° solidifies under 150 atm., remaining solid. At 33° it solidifies at about 500 atm., and then fuses again at about 200 atm. Local solidifications here suggest the occurrence of isomers or other impurity. Sometimes, as in the case of naphthalene, the volume-lag is not thoroughly static, but becomes viscous in character, &c. I have yet to study the effect of temperature on the magnitude of the volume-lag, *i.e.* on the difference of pressures isothermally corresponding to solidification and to fusion. Very large pressure-intervals are essential for this purpose.

at identical stress-points needs not be in the same chemical condition while stress is being removed, in which it was when stress was being applied ; for there will be certain groups of particles, uniformly distributed throughout the solid, which during the "stress on" phase pass from a first molecular condition to second, and which, in virtue of the volume-lag, do not regain their original state at identical pressures of the "stress off" phase. The march in the two cases is not a symmetrical one. This I take to be the inherent nature of the phenomena studied by Cohn*, Warburg†, and others, and to which Ewing‡, after much original research, has given the generic name hysteresis. In my note I pointed out the important bearing of the volume-lag on the molecular behaviour of matter§, though I have yet to specify my views in detail. The occurrence of hysteresis, therefore, implies a favourable molecular mechanism of the kind indicated, and one would not expect to find it at once in all substances.

Conformably with the above, the interpretation given by Mr. C. A. Carus-Wilson‖ of his important discovery (to which I alluded in a former paper), is much more than an analogy.

27. Warburg and Ewing have proved that hysteresis is not only associated with mechanical stress, but may be very clearly evoked by magnetic stress. Curiously enough, the evidence in favour of the views expressed in § 26 is here directly forthcoming. Remsen's¶ discovery of the chemical influence of the magnetic field, additionally substantiated as it now is by the ingenious experiments of Rowland and Bell**, proves beyond a doubt that magnetic iron is more electronegative than unmagnetic iron. Conformably with the above paragraphs, I therefore infer that this phenomenon is to be interpreted as directly evidencing a chemical difference between magnetic and unmagnetic iron, and as such I consider it an exceedingly important step towards an ion theory of magnetism††. Thus the occurrence of the chemical difference in

* E. Cohn, Wied. *Ann.* vi. p. 388 (1878).
† Warburg, Wied. *Ann.* xiii. p. 141 (1881).
‡ Ewing, Phil. Trans. ii. p. 545 (1885).
§ American Journal, xxxviii. p. 408 (1889).
‖ Carus-Wilson, Phil. Mag. xxix. p. 200 (1890).
¶ Remsen, American Chemical Journal, iii. p. 157 (1881).
** Rowland and Bell, Phil. Mag. [5] xxvi. p. 105 (1888).
†† In 'Nature' (xli. p. 370, 1890) I pointed out that closed helical paths of molecular dimensions, each consisting of a right- and a left-hand screw-thread, with their ends joined, can be generated by the symmetrical interpenetration of two congruent Bravais nets. I inferred that electrical charges urged along and around the said closed helical paths by the action

question, and the explanation of magnetic hyteresis, as given in the present and preceding paragraphs, mutually sustain each other.

28. Whether viscosity and dissociation in solids are to be explained with reference to a single mechanism, or whether we are to conceive of two mechanisms (molecular and atomic frameworks), one, as it were, within the other, is at the present stage of research a mere question of special convenience. The remarkably low viscosity at the yield-points of metals, as well as the similarly low viscosity near the Gore-Barrett phenomena, are both in conformity with the sudden passage from a first molecular state to a second, through an instability.

29. It follows from Tables I. to VIII., that in an æolotropically strained transparent solid like glass, electric conduction is different in different directions, the difference depending on the intensity of strain. Suppose this be considered in connexion with the doubly refracting property of such a solid, and again with Warburg and Tegetmeier's* researches on the electric conduction of quartz along its optic axis, with non-conduction at right angles to it. Then the inference is tenable, that the strain artificially sustained in one case is naturally sustained in the other. Tegetmeier's conducting sodic silicate, ingrained in the crystalline structure of quartz, and possessing larger molecular conductivity in quartz than

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of the magnetic field, could be made to replace the usual conception of molecular currents circulating in a molecule without resistance. From this point of view magnetic and electric fields merely differ in the rotational character of the former as compared with the non-rotational character of the latter. Whereas in an electrolyte the ion-dissociation takes place as the result of chemical relations and heat, it takes place in a metal under the mere influence of heat. The immediate action of both fields is directional; and by taking advantage of the positions of labile equilibrium of the ion, they act in a way analogous to Clerk-Maxwell's demons ('Heat,' chap. xxii. § 10), producing marked effects at the expenditure of a relatively small amount of work.

The advantage which I seek for in this tentative suggestion has direct reference to my own line of work. I can picture to myself the role played by the *foreign* ingredient chemically present in iron, in modifying the retentiveness and the magnetic stability of the metal. Thus I conceive the carbon atoms in hard steel to be so placed that after magnetization they block out definite closed helical paths in the metal, along which the transfer of charges must thereafter take place. Hence an increase of magnetic stability as contrasted with pure iron, where from any point four or more such paths may be open. Again, other substances (manganese, say) may be conceived to unite with the iron in such a way as to shut out the possibility of closed helical paths altogether. The fact that my permanent magnet is essentially a self-exhausting engine does not seem to be a serious objection.

* Warburg and Tegetmeier, Wied. *Ann.* xxxv. p. 455 (1888); xli. p. 18 (1890).

in glass, may be looked to as responding to strain of the kind suggested.

30. In the next six paragraphs it will be convenient to discuss some of the errors relating to both the measurements of resistance and electromotive force.

The effect of pressure on the polarization occurring in case of the above cell and of exceedingly weak currents is somewhat difficult to handle. Warburg * and others have shown that the reaction is essentially Na/glass/Hg changing to Na/Na_2SiO_3 glass/NaHg, or a mere transfer of sodium through the walls of the glass, by aid of sodium silicate as a conveyancer. I shall therefore have to rely on the data of Table II., in which, if a marked effect of pressure on polarization had been present, it would have been detected. It will be remembered that I commenced with high initial pressures ($p_0=50$ to 200 atm.) to obviate incidental disturbances.

31. The effect of pressure on the oil in the piezometer was specially investigated in each case. *Cf.* Tables III. to VIII., § 38.

32. A source of error is introduced by the temporary shifting of the isothermal planes of the piezometer, during compression, in virtue of the compressibility of the oil contained in the tube. Adiabatic thermal changes during compression or removal of pressure would produce effects of a sign opposite to those of the Tables.

To remove both of these it was often my habit to wait 3 to 5 minutes, supposing the original thermal state was then nearly enough regained. Longer waiting was not safe because of fluctuations of the astatic system of the galvanometer.

Fig. 6.

Special tests were made as follows :—In fig. 6 let P Q be the piezometer closed at Q, and receiving pressure in the direction of the arrow. Let A B be the position of the glass resistance-tube. Finally, let the hollow cylindrical vapour-bath surrounding the piezometer stretch respectively from *b* to *d*, or from *a* to *c*, or from *c* to *e*. Parts lying within the vapour-bath have constant temperature, which falls off rapidly from both ends of the bath towards the ends of the piezometer. When pressure is applied the vertical isothermal planes of the compressible oil are all moved from

* Warburg, Wied. *Ann.* xxi. p. 622 (1884); xxxv. p. 455 (1888).

P to Q. With the vapour-bath in the position $b\,d$, pressure would thus cool the end A and heat the end B of the glass tube A B; but the cooling would exceed the heating. Hence an error of the sign of the data, Table I. &c. Now let the vapour-bath be shifted to the position $a\,c$ and the thermal state be steady. The B-half of the tube A B is now exposed to cold, and compression can only have the effect of heating these parts, seeing that the A-half is protected. Hence an error of a sign *opposite* to the data of Table I. &c. Finally, when the bath has the position $c\,e$, the error first considered would be accentuated.

I made experiments in accordance with this scheme at 310°, but found that this severe test did not change the character of the results of Table I. Data are superfluous. Again, decreasing the length of the tube A B had no appreciable effect. Similar tests were made with reference to Table II.

33. It is clear at the outset, since pressure increases both the resistance of glass and the electromotive force NaHg/glass/Hg, that changes of the latter will act in a way tending to wipe out the change of resistance. Let e, I, R denote the electromotive force, current, and resistance of the uncompressed circuit. Let I_p be the current corresponding to pressure p, and k_R and k_e be respectively the pressure-coefficients of resistance and electromotive force. Then

$$k_\mathrm{R}=(\mathrm{I}(1+k_e p)-\mathrm{I}_p)/p\,.\,\mathrm{I}_p. \quad . \quad . \quad . \quad . \quad (1)$$

Table II. gives $k_e=10/10^6$, say, whence the values of Table XI. result from Table I., series III. *cf.* § 11. In the final column $k'_\mathrm{R}=\delta\mathrm{R}/\mathrm{R}\,.\,\delta p$, the former coefficient.

TABLE XI.—Allowance for Increments of Electromotive Force. $\theta=215°$.

p.	$10^3 p\,.\,k_e$.	$\mathrm{I}(1+pk_e)$.	I_p.	$10^6\times k_\mathrm{R}$.	$10^6\times k'_\mathrm{R}$.
523	5·2	21·18	19·47	168	157
995	9·9	21·28	18·11	175	164
1411	14·1	21·37	17·27	168	156
512	5·1	21·18	19·39	180	169
1016	10·2	21·28	18·07	172	163
1403	14·0	21·37	17·28	169	156

Thus the data underlying §§ 22, 23, 24 are accentuated. At 310° a permanent pressure-coefficient k_e could not be detected, and at 100° it is certainly very much in error (§ 34). Since therefore k_e is never fully vouched for, I have omitted it in the computation of k_R altogether.

34. In case of an uncompressed circuit shunted by unavoidable leaks, let R_1, R_2, R_3 be the resistances of the cell, the shunt, and the metallic circuit respectively. Similarly let i_1, i_2, i_3 be the three partial currents corresponding respectively to R_1, R_2, R_3. Let $\delta R_1/R_1$ be the effect of pressure on the resistance of the cell (resistance-tube), and $\delta e/e$ be the simultaneous increment of electromotive force. Finally, in case of the compressed circuit, let accentuated symbols replace the symbols for the uncompressed cell. Then a somewhat tedious reduction leads to

$$\delta R_1/R_1 = \frac{i_3(1+\delta e/e) - i_3'}{i_3'} \frac{(1+R_2/R_1)(1+R_3/R_1)-1}{R_2/R_1-(n-1)R_3/R_1}, \quad . \quad (2)$$

$$\delta e/e = \frac{i_3'}{i_3} \frac{(\delta R_1/R_1)(R_2/R_1-(n-1)R_3/R_1)}{(1+R_2/R_1)(1+R_3/R_1)-1} - \frac{i_3-i_3'}{i_3}, \quad . \quad (3)$$

where $\delta R_1/R_1 = n\delta R_2/R_2$, and $\delta R_2/R_2$ is the pressure-coefficient of the oil through which the leakage obviously takes place. Regarding $\delta R_1/R_1$ in (2), if the resistance, R_3, of the metallic circuit is relatively small, or if R_1 be reasonably small relative to the leak R_2, the considerations of § 27 at once apply. The case of $\delta e/e$, however, is serious. Supposing, again, that R_3/R_1 and R_1/R_2 are small, the last equation reverts to

$$-\delta e/e = (i_3 - i_3'(1+\delta R_1/R_1))/i_3,$$

and thus the changes of resistance due to pressure are interpreted as changes of electromotive force. Even zero or electrometric methods will only measure the difference of potential of two points of the leak-shunted circuit. Hence the permanent pressure-coefficients ($\delta e/e$) of Table II. cannot but be regarded with suspicion, and they are merely an essential justification of Table I. *et seq.*

35. A final difficulty in case of short-circuiting is not to be lost sight of. A leak usually includes an electrolyte between two different metals, and thus introduces an electromotive force in a way quite beyond computation.

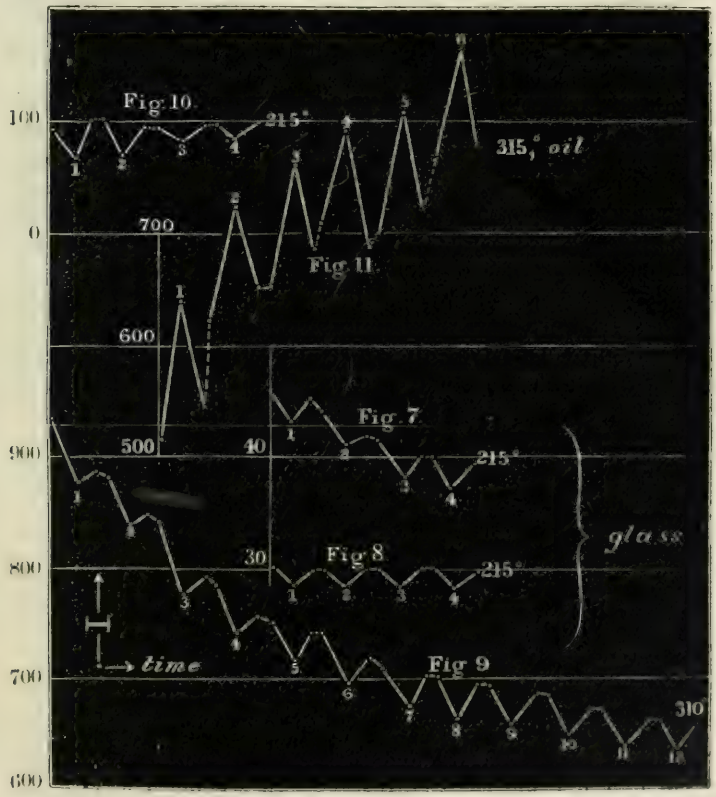
36. The consideration of the data of Table II. would now be in order: but for the reasons just stated I hold the work scarcely ripe for discussion, and will therefore withhold remarks until I can devise some more nearly faultless method of measurement.

37. In order to exhibit the full character of the individual observations of Tables I. to VIII., I shall discuss a series of data which I was first inclined to interpret as an electrical manifestation of volume "accommodation" (§ 17). In figs. 7 to 9 the observed intensities of current in relative

measure are given as ordinates. They are therefore inversely proportional to the resistance of the glass. The abscissæ are times, supposing that the times consumed in making each triplet of observations are equal and similar. The oscillations are due to the fact that pressure is raised from about 150 atmospheres to about 600 atmospheres, and then lowered to the first value again, thus giving the three points for each of the triplets numbered.

Figs. 7, 8, 9.—Charts showing the Oscillation of the Electric Conductivity of Glass with pressure, at 215°, 310°, and again at 215° respectively. Experiments made consecutively.

Figs. 10, 11.—Charts showing the Oscillation of the Electric Conductivity of very viscous Hydrocarbon Oil ("mineral machine-oil") with pressure, at 215° and 310° respectively.



In figs. 10 and 11 similar results are given for thick mineral machine-oil. In the former, pressure was twice increased from about 160 to 980 atmospheres and back again; and then

from about 160 to 540 atmospheres; thus obtaining amplitudes of different values. In fig. 11 pressure oscillated between about 150 and 600 atmospheres.

Figs 7, 8, and 9, which were obtained consecutively, show a gradual decrease of resistance to a limit, very obviously in fig. 7 at 215°, quite as obviously in fig. 8 at 310°, but not obviously, if at all, in fig. 9. Hence the inference is suggested that the continued exposure to strain alternations at 310° has wiped out all viscous instability possible at 215°. The volume-elasticity of the glass, so far as its chemical manifestations are concerned, is now constant. The objections to this interpretation are twofold:—In the first place the amplitudes of oscillation are constant throughout, *cæt. par.*, and do not converge to a limit. Again, the results for oil show similar phenomena, not very obviously in fig. 10, but marked in fig. 11, where both the negative pressure-coefficient and the resistance-decrease act together to invert the figure.

38. I have finally to refer to the results obtained with highly insulating liquids. It appears from these that the effect on resistance of an additional number of molecules splitting up in consequence of the removal of a fixed amount of pressure, decreases rapidly with the total number splitting up, where the decrease is to be taken in an algebraic sense and to include a march through zero. In the case of sperm-oil, gasolene, petroleum, thin and thick hydrocarbon machine-oil, the observed pressure-coefficients pass from positive towards or actually into negative values as temperature increases, and at a rate which for the same oil between 20° and 300° is nearly constant.

These rates ($\delta R/R \,.\, \delta p \,.\, \delta\theta$) are as follows:—

Table XII.—Rate of Thermal Variation of Pressure-Coefficient.

Sperm-oil.	Gasolene.	Petroleum.	Thin Mineral Machine-oil.	Thick Mineral Machine-oil.
$-3/10^6$	-9.10^6	-6.10^6	-7.10^6	-6.10^6.
		$-10/10^6$		

The figures therefore denote the change of the pressure-coefficient per degree Centigrade. In a general way it may be noted that this change is least in sperm-oil, where ions are present in greatest number.

Similar remarks were made in my earlier paper*, after an

* American Journal, xl. p. 222 (1890).

examination of mercury and solution of zinc sulphate. Both coefficients in this case were negative, and I was not prepared for the positive coefficients ($\delta R/R . \delta p$) so marked in the present paper. The data as a whole, therefore, show that it is not permissible to pass from one substance to another ; doubtless because the number of molecules which must split up per unit of area to discharge the field varies largely from substance to substance. Inferences are to be drawn from one and the same solvent, either electrolytically dissociated by temperature, or modified by the solution of some given substance, or both.

39. The remarks of § 38 are substantiated by the incidental results of Table VI., where the number of ions is increased by dissolved dirt. It agrees with the negative pressure-coefficient found for zinc sulphate (*l. c.*). Moreover, by keeping the thick machine-oil at 310° for two or more hours, I found that its resistance continually decreased, while the pressure-coefficient passed from indistinctly positive to pronounced negative values. Dissociation is here to be inferred.

I have only touched upon this question in passing ; but if it can be proved that the occurrence of negative pressure-coefficients is an index of solution, then metals may also be regarded as holding ions in solution. In general a sequence of changes of state or of molecule corresponding to gas-liquid, liquid-solid, may be regarded as crowded into the solid state, though the external manifestations are here no longer obvious at once.

40. The present research has been excessively tedious and elusive. Moreover the final values for the pressure-coefficient of glass (Tables VII., VIII.), although consistent, do not show the uniformity of values which I had hoped to reach. Nevertheless the results are marked, and unless there be some occult behaviour of polarization, I do not believe that I have been led astray in my inferences. In so far as my results are correct, they contain the first direct and connected evidence of the change of chemical equilibrium with strain.

Regarding the behaviour of liquid insulators like the hydrocarbon oils, the results found present many points of interest, and I have no doubt that a more systematic study of the subject than I have been able to make would throw much light on the details of the mechanism by which electricity is conveyed.

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Washington, D.C.

III. *On the Diurnal Variations of Magnetic Elements, as depending on the Method of Tabulation. By* WILLIAM ELLIS, *F.R.A.S., of the Royal Observatory, Greenwich*.*

THE interesting paper of Messrs. Robson and Smith, "On the Diurnal Variation of the Magnet at Kew," which appears in the August number of the Philosophical Magazine (page 140), includes a comparison between the diurnal inequality of the declination-magnet as determined at the Greenwich and Kew Observatories in the years 1870, 1871, 1872, 1883, 1886, and 1887.

The Kew results for the years 1883, 1886, and 1887 were determined by the authors of the paper by Wild's method, the hourly ordinates for about five quiet days in each month having been measured. Those for the years 1870, 1871, and 1872 had been previously determined by Mr. Whipple, Superintendent of the Kew Observatory, and by him communicated to the 1886 Report of the British Association Committee on Comparing and Reducing Magnetic Observations; and were, as Mr. Whipple kindly informs me, calculated from the records of four selected quiet days in each month of the three years. The results for the whole six years are thus in every respect comparative.

The Greenwich results with which those for Kew were compared were deduced, not from selected days, but from the records for all days excepting those, comparatively few in number, on which either the magnet was excessively disturbed, or the record from some accidental cause was wanting. Whenever results for all days are hereafter mentioned, it will be understood to be with this limitation. For the days thus employed a pencil line was drawn by hand through each photographic trace so as to represent the general form of the curve, neglecting its petty irregularities, but giving consideration to deviations of marked character. The hourly ordinates were measured from such pencilled line, and it is on the measures so made that the diurnal inequalities contained in the Greenwich volumes, and employed by Messrs. Robson and Smith, depend.

Comparing together the Greenwich and Kew results for declination, found in the way described, Messrs. Robson and

* Communicated by the Author.

Smith showed that there existed a periodical difference in the diurnal inequality, similar in character, and generally also in magnitude, in each of the six years treated. Mr. Whipple, in the British Association Report before alluded to, had previously pointed out the existence of this periodical difference in the three years with which he dealt, and suggested that it might be in some measure due to instrumental causes, and in some degree also to difference of geographical position, which considerations would apply equally to the comparison of the years 1883, 1886, and 1887; but how far such causes may have acted, it was impossible from a comparison of this kind to determine.

Circumstances have now, however, arisen which enable us to make a direct comparison of the two methods of tabulation.

In compliance with a request made by the Sub-Committee of the Kew Committee of the Royal Society, the Astronomer Royal has arranged to select, yearly, five quiet days in each month, to be generally adopted for the discussion and comparison of the diurnal inequalities of magnetism at the various British magnetic observatories, in consequence of which diurnal inequalities will now be determined at Greenwich for these selected quiet days, as well as for all days in the manner which has been so long employed. The work at Greenwich for the first year under this arrangement, that of 1889, having been lately completed, opportunity is now given for making a direct comparison of methods, a comparison in which the question of difference of instruments or of geographical position in no way enters. Viewing the interest attaching to this matter, the Astronomer Royal has kindly given me permission to communicate to the Philosophical Magazine the results arrived at for the year mentioned.

The present comparison has been made not only for declination, but also for the horizontal and vertical forces, and the results are contained in the accompanying Table. The diurnal inequalities on the two systems, and their differences, are given, in the case of declination in minutes of arc, and for the horizontal and vertical forces in parts of these forces. But in order to make the comparison between the several elements more complete, the differences have been further converted into metric measure, those of declination being expressed as westerly force, the unit employed in the Table being ·00001 of the metric unit. The metric differences are also exhibited in the form of curves, for comparison with the curves for declination given by Messrs. Robson and

Smith*. The Greenwich declination-curve is less bold than that of Messrs. Robson and Smith, but in other respects shows great similarity, both in form and in the position of the nodal points. The deficiency in boldness may be a peculiarity of the year under discussion, the epoch being one of minimum magnetic activity.

The periodical difference shown by Messrs. Robson and Smith to exist between the Greenwich and Kew diurnal inequality of declination, as deduced at Greenwich from all days and at Kew from quiet days, thus appears to depend on difference in the character of the records employed; since the discussion of Greenwich records alone, on the two systems mentioned, leads to the same conclusion, not only as regards declination, but also for the horizontal and vertical forces. A difference of the same general character is shown in each element in all months of the year: these particulars could not well be given here, but it has been thought interesting to add in the Table the summer and winter effects, taking summer as including the months from April to September, and winter the remaining months of the year.

The records used in the formation of the Greenwich all days' results contain many irregularities which are smoothed in the way before mentioned. The quiet days, in 1889, contain practically no irregularities. It might thus be conjectured that something may be due to systematic bias in the performance of the smoothing operation; but it could, if necessary, be shown that no influence of this kind would produce differences so dissimilar in character for the different elements; besides which irregularities in the vertical-force record are so infrequent, and in the year treated so few and trifling, that practically no smoothing had to be done; but yet the curve for vertical force, as may be seen, is quite as pronounced as those for either of the other elements, and indeed forms a very much larger proportion of the whole diurnal inequality for vertical force (see the Table) than is the case for either of the other elements.

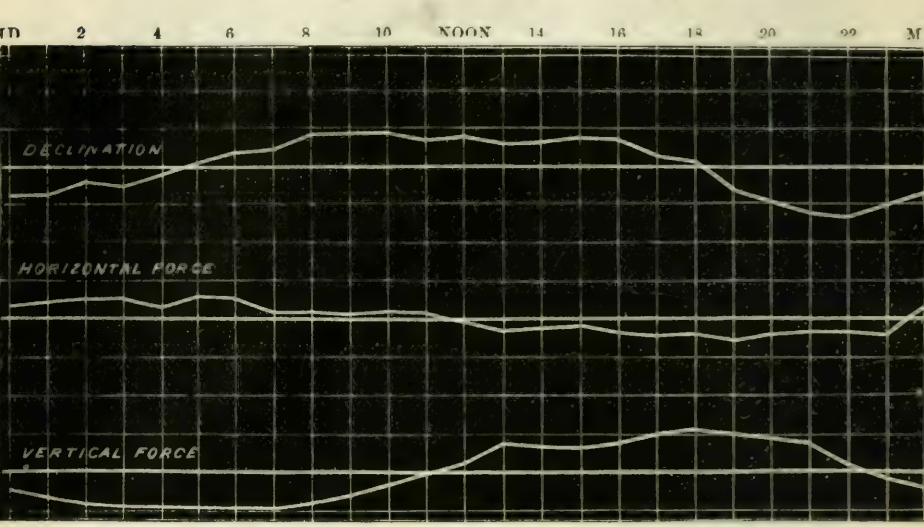
The difference between the two methods of determining diurnal inequality thus appears to arise from a physical cause, the form of the diurnal inequality-curve found by including all days differing in a systematic way from that given by using selected quiet days, in the manner shown in the diagram. The nodal points in the horizontal-force and vertical-force

* The vertical divisions on the diagram correspond each to ·00025 metric or ·00025 C.G.S. measure, equivalent on the declination-curve to 0′·47 in arc, whilst those on Messrs. Robson and Smith's diagram represent each 0′·40.

Royal Observatory, Greenwich.—Diurnal Inequalities of Magnetic Elements in the year 1889, as deduced from all days, and from five selected quiet days in each month, compared.

1889.	Midn.	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	Noon.	13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.
Declination, West.																								
Year: for all days	−1′31	−1′05	−0′86	−0′92	−1′07	−1′32	−1′49	−1′68	−1′82	−1′41	−0′07	+1′86	+3′57	+4′22	+3′76	+2′67	+1′59	+0′65	+0′05	−0′48	−0′91	−1′24	−1′24	−1′40
„ five selected days.....	−0′91	−0′69	−0′68	−0′70	−0′99	−1′36	−1′67	−1′92	−2′20	−1′78	−0′44	+1′57	+3′21	+3′92	+3′45	+2′32	+1′27	+0′49	+0′02	−0′19	−0′49	−0′62	−0′68	−0′68
„ excess of former	−0′37	−0′36	−0′18	−0′22	−0′08	+0′04	+0′18	+0′24	+0′38	+0′37	+0′37	+0′29	+0′36	+0′30	+0′31	+0′35	+0′32	+0′16	+0′03	−0′29	−0′45	−0′62	−0′56	−0′72
„ in metric measure ...	−20	−19	−10	−12	−4	+2	+ 9	+13	+20	+20	+20	+15	+19	+16	+16	+18	+17	+ 8	+2	−15	−24	−33	−35	−25
Summer: excess, metric ...	−18	−24	−15	−15	−9	−4	+ 8	+12	+15	+17	+17	+16	+22	+18	+18	+24	+22	+12	+2	−13	−21	−31	−35	−26
Winter: excess, metric	−21	−14	− 5	− 7	+1	+7	+11	+14	+25	+22	+22	+14	+16	+13	+15	+13	+13	+ 5	+1	−17	−27	−35	−35	−25
Horizontal Force.																								
Year: for all days	+18·8	+17·5	+14·1	+10·7	+9·3	+8·6	+1·7	−13·3	−36·9	−65·6	−80·2	−75·4	−50·2	−19·2	+3·4	+15·2	+18·1	+21·9	+35·3	+41·3	+38·7	+33·5	+25·9	+23·7
„ five selected days ...	+14·4	+11·7	+ 6·8	+ 3·4	+5·4	0·0	−5·8	−15·8	−39·7	−66·3	−82·2	−76·2	−49·1	−15·3	+6·4	+16·8	+22·2	+30·1	+40·5	+49·5	+44·7	+38·8	+30·9	+29·3
„ excess of former ...	+4·4	+5·8	+ 7·3	+7·3	+3·9	+8·6	+7·5	+2·5	+2·8	+0·7	+2·0	+0·8	−1·1	−3·9	−3·0	−1·6	−4·1	−5·2	−5·2	−8·2	−6·0	−5·3	−5·0	−5·6
„ in metric measure ...	+ 8	+11	+13	+13	+7	+16	+14	+5	+5	+1	+4	+2	−2	−7	−6	− 3	− 8	−10	−10	−15	−11	−10	− 9	−10
Summer: excess, metric ...	+10	+12	+ 9	+15	+6	+12	+ 5	0	+4	−4	+1	+2	−1	−7	−5	−3	− 5	0	− 5	− 4	−12	− 9	−10	−10
Winter: excess, metric	+ 6	+ 9	+18	+12	+8	+20	+22	+9	+7	+6	+6	+1	−3	−7	−6	−3	−10	−19	−14	−26	−10	−10	− 8	−10
Vertical Force.																								
Year: for all days	−2·0	−3·0	−5·2	−4·3	−1·5	+0·7	+0·3	+1·7	−0·6	−6·8	−12·8	−18·2	−19·9	−12·4	−1·6	+7·0	+12·9	+15·7	+15·6	+13·1	+10·7	+7·6	+2·7	−0·8
„ five selected days ...	+0·6	+0·5	−1·4	+0·5	+3·2	+5·7	+5·6	+7·2	+4·0	−3·7	−10·8	−17·9	−21·3	−16·5	−5·3	+3·4	+ 8·5	+10·0	+ 9·7	+ 7·2	+ 5·4	+3·6	+1·7	+0·2
„ excess of former	−2·6	−3·5	−3·8	−4·8	−4·7	−5·0	−5·3	−5·5	−4·6	−3·1	−2·0	−0·3	+1·4	+4·1	+3·7	+3·6	+4·1	+5·7	+5·9	+5·8	+5·3	+4·0	+1·0	−1·0
„ in metric measure ...	−11	−15	−17	−21	−21	−22	−23	−24	−20	−14	− 9	−1	+ 6	+18	+16	+16	+19	+25	+26	+25	+23	+18	+ 4	−4
Summer: excess, metric ...	− 4	−11	−17	−23	−28	−31	−31	−37	−31	−24	−13	+6	+17	+27	+24	+15	+23	+25	+24	+25	+29	+26	+12	−2
Winter: excess, metric	−18	−19	−16	−19	−13	−12	−15	−10	− 9	− 4	− 4	−7	− 4	+ 9	+ 9	+17	+16	+25	+28	+27	+17	+10	− 3	−6

curves it will be seen occupy nearly similar positions, rise of the horizontal-force curve being accompanied by fall of the vertical-force curve; the nodal points for declination occupy an intermediate position. As regards the comparative magnitude of the deviations, the range (difference between the greatest and least) is, for declination 1′·04 (+0′·38 to −0′·66), or in metric measure 55 (+20 to −35); for horizontal force, metric, 31 (+16 to −15), and for vertical force 50 (+26 to −24). The sums of the twenty-four hourly deviations,



metric, taken without regard to sign, are for declination 392, for horizontal force 200, and for vertical force 398.

It is remarked by Messrs. Robson and Smith that the range of the diurnal inequality in declination in each of the three years 1883, 1886, and 1887 is less at Greenwich, including all days, than at Kew for quiet days, by 0′·5, 0′·3, and 0′·5 respectively, as though magnetic irregularities tended to diminish instead of increasing the diurnal range. In the following Table there is given, in addition to the diurnal range (difference between greatest and least), the sums of the twenty-four hourly deviations from the mean, taken without regard to sign.

Greenwich Magnetic Diurnal Inequalities, 1889.

Element.	Range.			Sums of 24 Deviations.		
	All days.	Quiet days.	Excess all days.	All days.	Quiet days.	Excess all days.
Declination, in minutes ...	6'·04	6'·12	−0'·08	36'·83	32'·58	+4'·25
Declination, metric	320	324	− 4	1952	1727	+225
Horizontal Force, metric...	221	240	−19	1240	1277	− 37
Vertical Force, metric.....	156	137	+19	774	673	+101

Thus, comparing Greenwich values only, we find for 1889 mean of the three values of excess under Range $= -1$, and the mean under Sums of Deviations $= +96$. The latter is probably a better indication than the simple range of the influence of magnetic irregularities on the diurnal inequality formed from all days. But the discussion of the records of other years will throw further light on this point.

The question whether, in forming diurnal inequalities, all days should be employed, or selected days only, is one that has forced itself into notice in the discussion also of meteorological elements. For instance, in air-temperature, the ordinary diurnal change is in winter, at times, quite reversed, and the barometric movements are sometimes large and very irregular. But yet all days have been usually included in determining diurnal inequality. It may be questionable whether it is proper arbitrarily to reject days because they appear to be affected with irregularities which may themselves have a diurnal period. Indeed, considerable variation in amplitude of motion may be found to exist in magnetic registers on different quiet days in the same month. Considering, however, the amount of work involved in the tabulation of all days, the proposal to discuss the records of British magnetic observatories for five selected days monthly, in each year, will make a practical beginning in that which in magnetism is so much required—the tabulation of the records of different observatories on one uniform plan, in order to effect a more efficient and trustworthy comparison of results.

IV. *Additional Notes on Secondary Batteries.* *By* Dr. J. H. Gladstone, *F.R.S.*, *and* W. Hibbert, *F.I.C.**

During the publication of a series of papers by Dr. Gladstone and Mr. Tribe in 'Nature,' 1882, on the "Chemistry of the Planté and Faure Accumulators," a discussion arose as to whether the sulphate of lead, to which they attributed so important a part in the reaction, could be reduced by electrolysis. It was shown at the time by experimental proof that this was possible, even when the sulphate of lead was pure, and it was contended that when intimately mixed with peroxide of lead, as in actual practice, there was no difficulty about the matter †.

There arose, however, a belief that a subsulphate of lead was produced on the plates. Some experimenters found in this belief an explanation of the difficulty in reducing those masses of salt which occasionally form in practice, while others looked upon the subsalt as more easily reducible than the neutral compound.

So far as we are aware, no specimen of the supposed subsalt was described till Professor Frankland published his paper in the Royal Society's Proceedings, 1889, vol. xlvi. p. 304, in which he gives an account of what he believes to be two definite subsulphates. That produced from litharge we have already examined in our paper of last June ‡. Since then we have turned our attention to the other possible subsalt made by the action of sulphuric acid on minium.

In the original paper §, Gladstone and Tribe gave the formula of decomposition as

$$Pb_3O_4 + 2H_2SO_4 = PbO_2 + 2PbSO_4 + 2H_2O.$$

They showed by means of a quantitative experiment its gradual slow formation, and said, "It is evident that in a Faure battery we are dealing with plates that consist of a superficial layer of mixed peroxide and sulphate of lead."

Frankland, while viewing this red substance as a subsulphate, arrived at precisely the same ultimate composition.

* Communicated by the Physical Society: read November 28, 1890.

† See "The Chemistry of the Secondary Batteries" in 'Nature' Series.

‡ Phil. Mag. Aug. 1890, and Proc. Phys. Soc. x. p. 448.

§ See volume cited, p. 14.

which he expressed by the formula $S_2Pb_3O_{10}$. He adduces, however, no evidence to show that it is not a mixture of PbO_2 with $2PbSO_4$. We sought for some means of deciding between these two views. A solution of acetate of ammonium is known to dissolve sulphate of lead, and was in fact used long ago for that purpose. It might therefore be expected to separate the sulphate from the peroxide, while it was not so likely to bring about the decomposition of such a compound as $S_2Pb_3O_{10}$.

Some of the red substance was prepared by treating minium with an excess of dilute sulphuric acid (1 of acid to 10 of water). After four days the action was still incomplete, but eventually it absorbed the full amount of acid required by theory.

The percentage of lead in the resulting red substance was just over 72 per cent.

A portion of this, after treatment with a 3 per cent. solution of acetate of ammonium, left a residue which was much darker in colour than the original and contained 82 per cent. of lead. That is to say, it was approximating towards PbO_2, which contains 86·6 per cent. of lead. The liquid was colourless, and the ratio between the Pb and SO_4 dissolved was determined in several different instances. The ratio

$$\frac{\text{Weight of Pb}}{\text{Weight of } SO_4}$$

varied from 2·0 to 2·15, pure $PbSO_4$ requiring 2·16 and Frankland's compound 3·23. The portion dissolved therefore was not a basic sulphate, and the evidence tells against the original substance being a chemical compound.

Of course, it is impossible to affirm that no subsulphate is ever formed in the reactions of a secondary cell, but all that we actually know is perfectly consistent with the old and simpler supposition that $PbSO_4$ is the salt alternately formed and decomposed.

Action of Sulphuric Acid on Lead.

In our former communication we described a comparative experiment in which dilute sulphuric acid, either alone or mixed with a small quantity of sodium sulphate, was allowed to act on spongy lead. The experiment was allowed to continue for five months, and hydrogen gas was given off for

such a length of time that we thought it would be interesting to analyse the resulting substance.

The residue from the action of the pure acid on the lead consisted of 82 per cent. of sulphate of lead and 18 per cent. of metallic lead, while that from the action of acid mixed with sulphate of soda consisted of 89 per cent. of lead sulphate and 11 per cent. of metallic lead.

Although the action of the acid on the lead was initially diminished by the presence of sodium sulphate, the final result in this instance was rather the other way. No doubt the whole of the spongy lead would have been converted into sulphate if it had not been for the large amount of insoluble salt which protected the remaining particles.

This result throws light on the reason why a lead plate deteriorates during a long rest.

V. *On the Measurement of Electromagnetic Radiation. By* C. V. Boys, *A.R.S.M., F.R.S., Assistant Professor of Physics at the Royal College of Science, London*, A. E. Briscoe, *A.R.C.S., and* W. Watson, *A.R.C.S., B.Sc.**

[Plate V.]

At the time that Mr. Gregory described and exhibited his "Electric Radiation Meter"†, which indicated and measured electromagnetic radiation by the increase in length of a fine platinum wire stretched in a glass tube in consequence of the heat developed by the induced currents within it, one of us expressed the view that it would be interesting to confirm by some independent method the conclusion that the wire was lengthened by heat, as it was not absolutely certain, though exceedingly probable, that the increase in length might not be apparent only and not real.

The following is an account of experiments made by two independent methods, with the view of finding whether the expansion observed by Mr. Gregory was such as might be expected from the induced currents.

First Method.

Imagine two straight wires parallel and near together, but not touching one another or any conductor. Let them be placed parallel to and at a convenient distance from a cylindrical rod of the same length as either of the wires. Then, if electrical oscillations are started in this rod by any well-

* Communicated by the Physical Society; read June 20, 1890.

† Phil. Mag. Jan. 1890.

known method, the two wires will act as resonators, and induced oscillations will occur in them, not necessarily in absolutely the opposite phase to the oscillations in the primary, but at any rate in the same phase in the two wires, so that the electricity in each will surge up and down at the same time. If, then, the ordinary theories of electrodynamic and electrostatic action apply in the present case, which may be true or may not, then the currents going up together and down together will attract one another, while the charges resting chiefly at the two ends, being at one moment + above and − below, and at the next moment reversed, will repel one another. Owing to the harmonic distributions of the current and the charges, the electrodynamic attraction will be mainly in the middle parts, while the electrostatic repulsion will be mainly at the two ends. Further, both these distributions vary harmonically with the time, and are a quarter-period removed from one another; but the integral effect of each is equivalent to a steady force, and the quarter-period difference of phase has no influence as far as forces are concerned.

In order to realize what these forces are, and what are the relations between them, it will be necessary to consider them separately.

(1) *Electrodynamic Attraction.*—Let the wires be supposed to be very close together, so that the force felt by any element is almost entirely due to those elements of the other wire which are so close to it that the variation of the current strength in those elements along the wire is inconsiderable. Now, if the distance apart is d, if c is the strength of the current at any moment (measured electrodynamically), and if l is the length of the element, the force exerted by the other wire on this element will be $2\frac{c^2 l}{d}$ dynes. But as the current at any point varies harmonically with the time, the average force will be necessarily half the maximum force; therefore the average force on the centre elements will be $\frac{c^2 l}{d}$, if c is the maximum current at the centre.

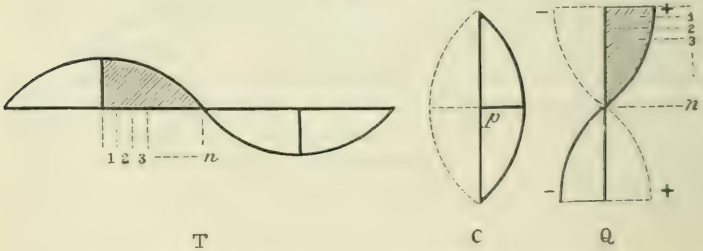
Since, also, the current varies harmonically along the wire, the average force per unit length over the whole wire will be half that at the centre; so that the attraction between the wires will be $\frac{c^2 \mathrm{L}}{2d}$, where L is the whole length of the wire.

(2) *Electrostatic Repulsion.*—In the same way, if q is the quantity of electricity (measured electrostatically) on

unit length at any part of the wire, the force of repulsion upon an element at any moment will be $2\frac{q^2 l}{d}$, the average force on this element will be $\frac{q^2 l}{d}$, and the total repulsion between the wires will be $\frac{q^2 \mathrm{L}}{2d}$.

Now to find the relation between these it is necessary to remember that the wires are resonators; that is, the oscillations follow the natural period and are not forced. Also that the total quantity of electricity on one half of the wire is the integral of the current that has passed the middle point. Although there is no difficulty in finding the relation between the attraction and repulsion, the following graphic method may be worth giving. In order to simplify matters, the resonator will at first be supposed of such a length that the oscillations occur at the rate of one a second, *i. e.* it will be supposed to be $\frac{1}{2}$ of 3×10^{10} centim. long; also the maximum current at the centre will be supposed unity. Now let the vertical line in C (fig. 1) represent the wire, and the distance of the harmonic curve from it at any point the strength of the current at that point when it is at a maximum.

Fig. 1.



In the same way, let the distance of the harmonic curve in Q from the wire at any point represent the charge at that point a quarter-period later, at which time it is at a maximum; then the total quantity on one end, represented by the shaded area, is the integral of the current which has passed the middle point *p*. Now this current varies harmonically with the time, as shown in the time-diagram T. This is divided into four equal parts. Thus the first represents (say) an upward current rising from zero to its maximum: this just neutralizes the previously charged wire. Then, in the second period, the continuation of the current produces an equal and opposite charge, which is a maximum when the current has become zero. In the third period, the current in the opposite

direction has again neutralized the charges by the time that it is a maximum ; and in the fourth period, it charges the upper end negatively and has ceased to flow when the negative charge is a maximum.

Now divide the second period of the time-diagram of current, T, into n ($=\frac{1}{4}$ of 3×10^{10}) elements, and the upper half of the wire in the quantity-diagram, Q, into the same number of equal parts, which will therefore each be one centimetre long. Now, since the total quantity of electricity represented by the shaded part in Q is equal to the time-integral of the current which is represented by the shaded part in diagram T; and since also each of these is bounded by a quarter-period of a sine curve, and is divided into an equal number of elements, it is clear that each space-element in Q, 1, 2, 3, ... n, must equal the corresponding time-element in T ; or, in words, though the quantity of electricity that has passed the point p in the first element of time is spread over the upper half of the wire in Q, and so on, yet at the nth element we may consider that that which passed during the first element of time is stored on the element 1, that which passed during the second element of time is stored on the element 2, and so on. Now, since the current-strength in the first element of time is 1, and since this element of time has been made equal to $1/(\frac{1}{3} \times 10^{10})$ second, the quantity of electricity on the end centimetre of wire is $1/(\frac{1}{3} \times 10^{10})$ electrodynamic unit, or 1 electrostatic unit. This will be repelled by the wire opposite with the same force as that with which the current in the centre element of one wire will be attracted by that in the other wire, both when each is at a maximum and through all the harmonic variations. In the same way, the next element near the end in Q will correspond to the next element near the middle in C, and so on over the whole length of each ; and so, since the electrodynamic attraction over every element in time and space is equal to the electrostatic repulsion in the corresponding element, removed both in time and space by a quarter period, the total force due to one is equal to the total force due to the other. If any other length of wire is taken, and of course its corresponding period, since the number or length of the elements in both T and Q must vary together, the same result will follow ; and if any other strength of maximum current is taken, the attractions and repulsions will be changed to an equal extent, and therefore, if two straight wires are placed so close together that the distance between them is very small compared to their length, they will, when their natural electrical oscillations are induced in them, on the whole neither attract nor repel one another.

It follows from this that, if the oscillations be forced and made too slow, the accumulation of charge on the ends will be greater for a given maximum current than it would be if the period were natural, and therefore the repulsion should overpower the attraction. In the same way, with too rapid vibrations the attraction should overbalance the repulsion. Also since, if the wires are not close together, the electrostatic repulsion will have fallen away in a higher ratio than the electrodynamic attraction, it would appear that resonators which balance when close should attract one another when at a distance, or that resonators subject to forced oscillations which repel when near might attract when at a distance.

Prof. Fitzgerald, when the above theory of the mutual action of resonators was put to him, at once suggested that if the molecules of a body were subject to electrical oscillations it would be possible to imagine a physical cause for their supposed attraction when far, and repulsion when close.

Fig. 2.
½ full size.

In order to test the matter experimentally, the wires were made of a cranked form, as shown in fig. 2, so that the ends were on one side of a vertical axis (dotted), and the middle part on the other side. Then, if one is held close to the other, and if the second one is free to turn about the vertical axis, the attraction of the centre and the repulsion of the ends should conspire to produce rotation in the same direction *.

The first experiment was made with a pair of copper wires each one foot long, bent so that the end parts were each $2\frac{1}{2}$ inches, the middle part 5 inches, and the horizontal part 1 inch. This was suspended in a glass jar by a quartz fibre, so that the vertical axis of rotation was halfway between the ends and the middle portion. An ordinary galvanometer-

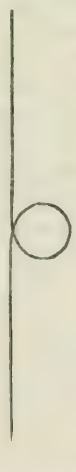
* It may be worth mentioning that the invention of this method was made in a particularly vivid dream, in which I found myself at the blackboard in the physical lecture-room, explaining that if the two wires were close together, the currents in each would be going up and down together, and so would attract one another, and that in order to make this attraction evident, the wire should be suspended near the axis of rotation, for the reason that where quartz-fibres can be employed there is a greater gain owing to the reduction of moment of inertia than loss by reduction of statical moment. I did not in the dream see that the charges should repel, or the necessity for the cranked form of wire. I may say that this was after Mr. Gregory had described his instrument, but the idea of looking for mutual attraction between a pair of resonators had not before occurred to me. C. V. B.

mirror was attached to the rigid glass hook from which the wire was suspended, and this could be seen through a plate-glass window in a torsion-box above the jar. The oscillator consisted of two pieces of brass tube half an inch in diameter with hemispherical ends, each 6 inches long in all. This was placed in a vertical position two or three feet away from the wires, and in the plane of the suspended wire, so that it should not act directly upon it. The two parts of the oscillator were connected by very fine wires with the terminals of a Voss machine. Then it was found that when the halves of the oscillator were separated too far for a spark to pass, there was no deflexion, while when they were gradually made to approach one another, no motion was visible on the scale until sparks passed, and then the motion was evident enough, the light even going in favourable cases off the scale in the right direction.

However, this was only a preliminary experiment made with materials at hand. It was clear that the material which was most suitable was that which had the highest conductivity for its density, namely, aluminium, and that only the outer surface of the wire could be efficacious, since the oscillations were at the rate of about 500,000,000 a second. Accordingly, thick aluminium wire was rolled into thin ribbon, which was then drawn through successive holes in a draw-plate until a perfect tube, cracked down one side of course, was formed.

We used resonators made of this material in the next experiments, which were made with the view of seeing whether the couple observed was due equally to the repulsion of the ends and attraction of the centre, or if one preponderated over the other. The fixed cranked resonator was then replaced by a straight one, which was held at first close and opposite to the ends of the suspended cranked resonator, when a strong repulsion was observed, as expected. It was then held in the corresponding position opposite the centre part, when, instead of the expected attraction, feeble repulsion was observed; and finally, on being placed equidistant from the two, the ends were repelled away.

Fig. 3.



Since this appeared to show that the electrostatic repulsion was much greater than the electrodynamic attraction, we tried the following experiment, in which the electrostatic action was reduced to practically nothing. A pair of resonators were made of the form shown in fig. 3, and one was weighted with a non-conductor and sus-

pended so that the straight part was in the axis of rotation. The other was then held with the curl close and parallel to the curl of the other, and so that at first the current in each should go round the same way, and then in opposite ways. No action was observed in either case. When also cranked or straight resonators were entirely immersed in water, no effect at all was observed.

We have given a short account of the early experiments because at first they were so completely in accord with the result of the theory put forward, though the action was more powerful than had been expected, that for a time we were deceived as to the real cause, and we wish to guard others from falling into what is after all a very obvious error. The later experiments showed either that the theory was only true as regards electrostatical repulsion, the electrodynamic attraction of the momentary currents being *nil*, or else that the results already obtained were spurious.

We have stated that the two resonators were suspended in a glass jar, outside which the primary oscillator was placed, and that while no repulsion was observed during the gradual charging of the oscillator-ends to a higher potential than that employed with the sparks, yet the moment the sparks passed when the ends were nearer together, the suspended resonator was observed to move in the expected direction. Now if the glass jar were a conductor, the oscillator-ends might be charged to any extent and no action would be felt inside ; if, on the other hand, it were a perfect insulator, then during the charging of the oscillator-ends before the spark the resonators would have induced charges in their ends which would make them repel one another. The glass jar exposed to the moisture of the air was a sufficiently good conductor, on its outer surface at any rate, to be able to screen the statical action of the charges on the oscillator-ends which were by the arrangement only slowly made to vary, and so the repulsion which might have been looked for was not observed ; but the moment a spark passed in the primary, the conditions were changed. The fall of potential was instantaneous, but the screening charge on the glass surface, which the previous moment produced within the jar an effect equal and opposite to that of the charges on the oscillator-ends, was unable instantly to disappear owing to the imperfectly conducting surface of the damp glass, and thus at this moment the resonators were in the condition that they would have been in had there been suddenly developed on the oscillator-ends equal and opposite charges, but with no glass jar between. This then was the cause of the repulsive impulse which was observed at each spark when they followed one another at

intervals. When, however, a torrent of sparks was produced, the glass surface would take up a screening charge equivalent to the mean charge on the oscillator-ends ; then, when the oscillator-ends had charges either above or below the mean charge, the statical action on the resonators would be the same as that due to the excess or defect on the oscillator, so that the steady repulsion observed was due to induction alone, and had nothing whatever to do with electrical oscillations proper.

In order to perfectly screen off this induction effect, and yet leave the action of the true electrical oscillations, it was necessary to so increase the conductivity of the surface of the glass jar that it would have time to acquire a screening charge which should follow variations of potential accompanying the sparks at the rate of, say, 10 or 20 a second, and yet leave it so imperfect as to be practically an insulator to oscillations at the rate of 500,000,000 a second, which corresponded to the apparatus in use.

Prof. J. J. Thomson has shown* that the conductivity of liquids may be determined by finding what thickness of a sheet of liquid is just sufficient to prevent oscillations of a known rate from exciting a resonator on the other side, and that the thickness must be proportional to the specific resistance. For instance, he found that a layer of dilute sulphuric acid three or four millimetres thick was just opaque to oscillations at the rate of 100,000,000 a second. It would therefore require a greater thickness to be opaque to oscillations of 500,000,000 a second, and a very much greater thickness for water to be opaque to oscillations of this rate. A duster, therefore, soaked in water, though it might reflect some fraction of this radiation, should be practically transparent to it. Nevertheless a wet duster would be amply sufficient to screen the action of true harmonic variation of potential of the frequency of the sparks, *i. e.* 10 or 20 a second. As a matter of fact, these variations of potential are not simply harmonic, but since by Fourier's principle the non-harmonic periodic change is equivalent to a series of true harmonic changes at successively higher rates all superposed, the wet duster should completely screen all the lower of these components up to a certain point, and probably far enough. On wrapping up the jar with a wet duster all effect was found to cease, and the spurious character of the deflexions was demonstrated. It is possible that these are not the only experiments with electrical oscillations in which a wet duster or its equivalent might be found of service.

The apparatus was then remade with the view of obtaining

* Proc. Roy. Soc. vol. xlv. p. 269.

very great delicacy. To make the resonators aluminium wire was rolled into ribbon of ·2 × ·001 centim., so that each centimetre in length weighed only half a milligram. Two pieces 30 centim. long were fastened in the cranked form previously described on very light frames made by cementing to almost capillary thin glass tubes cross bars cut from microscope cover-glass, so that the ends of these cross bars held the corners of the cranked pieces of aluminium ribbon. One of these was suspended in the same apparatus by a fine quartz fibre, and all was arranged with the view of obtaining a delicacy comparable with that employed by one of us in the Cavendish experiment. It was now impossible to keep the spot of light at rest, owing mainly to air-currents in the jar set up by differences in temperature of the sides of the jar which could not be avoided in the schools, and also to the perpetual tremor. In the winter, however, the elementary laboratory on the other side of the Exhibition Road was not being used, and so everything was transferred to a small room there, where a fair degree of quiet and uniformity of temperature could be obtained. The Voss machine was replaced by a large induction-coil, which gave a greater torrent of sparks. Then, to get more energy in each spark, the primary oscillator, made of 12 millim. tube, was replaced by a pair of spheres 100 millim. in diameter, with small spheres on short sliding rods, between which the sparks passed. The scale was placed at a distance of 281 centim. from the mirror. Then, when the wet duster was placed round the jar and the sparks made to pass, deflexions of 5 to 10 millim. were observed. Fearing, however, that even the wet duster failed to completely screen the induction-effects due to the rise and fall of potential of the primary or rather some of the higher harmonics already alluded to, we soaked it in dilute sulphuric acid instead of water, so that no doubt should exist as to its sufficient conductivity to quench the sham effect while it still remained unable to stop more than a small proportion of the waves of 500,000,000 a second. With this precaution all definite movement of the spot of light ceased. It was seldom that air-currents did not cause a gentle hovering of the index a few millimetres either way, which, however, had no relation to the starting or stopping of the sparks; on one or two frosty days, however, when the temperature was very uniform, there being no fire, the spot of light was so steady that a movement of even $\frac{1}{10}$ millim. on the scale would have been observed, but we have based our calculation on the certainty that the deflexion was not $\frac{1}{5}$ millim.

In order to make sure that this was a true negative result the duster was removed, when at once the index was driven

violently off the scale, and then a Hertz resonator tuned to the oscillations of the primary was placed in the jar and surrounded by the same acid duster when the sparks in the gap were evident, showing that the proper electromagnetic waves did penetrate into the jar as supposed.

The turning moment corresponding to a deflexion of $\frac{1}{5}$ millim. may be found from the following particulars :—

Period of oscillation of mirror and stem (oscillator removed), ·947 second.

Period of oscillation with wire ring hung on, 4·13 second.

(Wire ring 1·6 centim. diameter outside, made of wire ·122 centim. in diameter; mass ·4635 gramme.) Hence

$$\text{Couple} = 1{\cdot}1 \times 10^{-5} \text{ C.G.S. units, and}$$

$$\text{Average value of couple} = 3{\cdot}7 \times 10^{-7} \text{ C.G.S. units per centim. of wire of resonator,}$$

which corresponds to a force of about 3×10^{-7} dynes, since the distance from the axis is $1\frac{1}{4}$ centim. This is less than a two-hundred-millionth of the weight of a grain, or a three-thousand-millionth of the weight of a gramme.

Since the wires were only ·2 centimetre apart, this shows that, if the currents in the wires, instead of being oscillating, had been simply ordinary steady currents, those currents could not have reached the value of ·00017 C.G.S. electromagnetic unit or ·0017 ampere.

Now the moment, if the theory advanced is correct, is due partly to electrostatic repulsion and to electrodynamic attraction which are equal to one another, but owing to the harmonic distribution of both, both in time and in position, and owing to the fact that the weaker part of each of these forces is tending to counteract the stronger part, the total average resultant force is by no means double or even equal to that due to a steady current alone of a strength equal to the actual maximum.

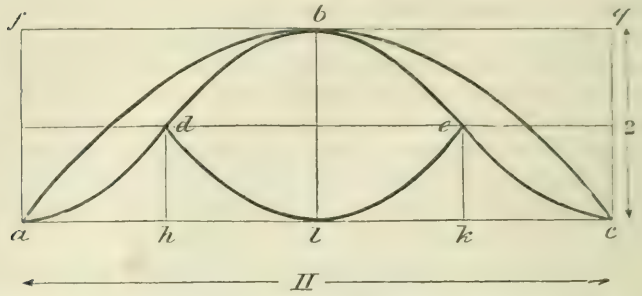
To find the relation it is necessary to first consider the effect of the harmonic distribution of either, say the current, along the wire. The square of this at any point is a measure of the force at that point, so that the force varies from zero at the ends to its full value in the middle, having passed its half value at the points where the wire crosses the axis of rotation.

Thus, in fig. 4, the ordinates of the upper curve $a\ b\ c$, which is half a sine curve, represent current strength, those of the lower curve $a\ d\ b\ e\ c$, which is a complete sine curve on half the scale, but shifted vertically by the amount of its own maximum ordinate, since

$$\sin^2 a = \frac{1 - \cos 2a}{2},$$

represent the force due to the current at each point. The rectangular area $f\,g\,c\,a$, equal to 2π, measures the total force

Fig. 4.



due to a uniform current of the maximum value. The areas $a\,d\,h$ and $c\,k\,e$ are the forces due to the ends of the wires in the wrong direction, and these together

$$= \frac{\pi}{2} - \int_0^{\pi/2} \sin\theta\, d\theta = \frac{\pi}{2} - 1.$$

The area $h\,d\,b\,e\,k$ is the force due to the middle half of the wire in the right direction, and this

$$= \frac{\pi}{2} + \int_0^{\pi/2} \sin\theta\, d\theta = \frac{\pi}{2} + 1.$$

The difference of these, which is the area $d\,b\,e\,l$, is the balance in the right direction, and this $=2$. But the force due to a current of the maximum strength over the whole length of the wire is 2π, so the force in the cranked conductor due to the harmonically distributed current and the opposite effect of the ends is $\frac{1}{\pi}\times$ that due to uniform maximum current over the whole wire. The current is not steady, but varies harmonically with the time, so on this account the value must be halved again, but this halving is exactly balanced by the doubling which results from the fact that the electrostatic exactly equals the electrodynamic effect.

We have seen that the force was not so great as that due to a steady uniform current of ·0017 ampere: therefore the maximum current in the centre could not, if the oscillations continued uninterruptedly, have reached the value of $\sqrt{\pi}\times$ ·0017 or ·003 ampere. Since in the most violent torrent of sparks that can be produced the time during which the oscillations

last is very small compared to the interval between two sparks, it is quite possible, and even probable, that the actual current during the earlier part of each spark greatly exceeded this, but this is a superior limit to the value of the square root of the mean square of the strength of the current in the particular case.

It should be noted that two errors, each of which is numerically insignificant, have, for convenience, been made. One is the supposition that the forces on the elements near the ends of the resonators are the same as though they were continued together with the stationary wave. As a matter of fact, it is only the last few millimetres for which there is a falling off. The second error is made by supposing that the middle half of the wire is all at one distance from the axis on one side, and the two end quarters at an equal distance from the axis on the other side. As a matter of fact, the wire has to cross over, but as the two forces almost exactly balance on the small part which crosses the axis, it was not worth while to complicate the simple statement of conditions illustrated by fig. 4 for the sake of an imaginary degree of accuracy which the nature of the observations would not justify.

Second Method.

As the first method, carried out with all the delicacy which under the conditions we could make use of, gave no promise, we determined to find by some direct process whether the heat which Mr. Gregory had inferred from the expansion of the wire was real. For this purpose we made use of one of the most delicate heat-measuring instruments that exist, which is specially suitable for detecting very small quantities of heat diffused over a great length of wire, namely the convection air-thermometer of the late Dr. Joule*. With this instrument he was able to detect the direct heating-effect of the moon's rays unconcentrated by lens or mirror.

His instrument consisted of a tube about 2 feet long and 4 inches in diameter, divided longitudinally by a blackened pasteboard diaphragm, leaving spaces at the top and bottom. In the top space a piece of magnetized sewing-needle, furnished with a glass index, was suspended by a single silk fibre. Any excess of temperature on one side of the partition caused an air-current, which at the top passed from the hot to the cold side and deflected the needle.

* Proc. Manchester Phil. Soc. vol. iii. p. 73.

We have made use of Joule's instrument, not exactly in the original form, but with two classes of index, and with an essential improvement which makes it extraordinarily sensitive without greatly affecting its simplicity. The first class of index depends for its working on the fact that when a small piece of phosphorus is placed in air it gradually oxidizes, and the oxide formed slowly falls, if the air is still, in a well-defined column, appearing like smoke. If there is any very small motion of the surrounding air, this column of phosphorous oxide will be deflected. It thus forms an excessively delicate and light index for detecting movements in the air.

To overcome the difficulty of keeping the index at rest, owing to radiation from neighbouring bodies or to draughts of varying temperature, we have surrounded the divided tube by another, which was kept rotating continuously by clockwork. If any part of this guard-tube becomes slightly heated, it is carried round and made to heat the instrument equally all round, and so it produces no effect.

As the determination on theoretical grounds of the most suitable dimensions presents considerable difficulties, we decided to make a series of tubes of different sizes and compare their sensibility. The object of the instrument being to measure the heat developed by the electromagnetic radiation in a wire within the instrument, it was necessary to make both the tube and guard-tube of some insulating material, such as glass.

The tube to be used was cleaned, and a roll of brown paper about 1 inch long was pasted round one end. This fitted tightly into a mahogany ring, D (Plate V. fig. 5). The tube was divided longitudinally by a partition of cardboard (F), which was made to fit tightly into the tube. This partition extended from the bottom to within about an inch of the top, which end was closed by a cork.

The projecting end of the mahogany ring (D) fitted into a corresponding hole in a piece of wood (E), which was itself supported on two blocks (A and B). The tube (represented by the dotted circles in the plan, fig. 6) came directly over this space between A and B, the partition being parallel to their adjacent faces.

Between A B, and immediately beneath the tube, two glass semi-cylinders were placed, with their convex surfaces facing each other. They are shown in plan in fig. 6 (M N), and one is shown in perspective in fig. 7. At 2 centim. from the top of one of these semi-cylinders a small paper scale (fig. 5), divided in half-millimetres, was attached. When a current

of air passes from one side of the tube to the other, it has to pass through the narrow space between these cylinders.

A hole was bored through the top of B, through which a capillary glass tube could be passed. This tube was filled with phosphorus, and the glass broken away for about one millimetre, so as to expose a clean piece of phosphorus whenever the stream of oxide had to be observed. The tube was then passed through the hole (K), so that the exposed piece of phosphorus came just beneath the partition and between the glass cylinders. It is shown in place at H in fig. 5.

By this means the stream of phosphorous oxide was formed at the narrowest part of the air channel, and so was affected to the maximum extent by any passage of air from one side of the partition to the other. The resulting deflexion of the phosphorous-oxide stream could be read with an accuracy of about one-tenth millimetre. In this form, when the phosphorus index is deflected it is carried to a part where the channel is much wider, owing to the curvature of the glass half-cylinders. On this account the deflexion of the index is not any simple function of the rate at which the air is passing. With a view to do away with this want of proportionality, and also, if possible, to render the instrument more sensitive, the glass half-cylinders were replaced by a pair of narrow flat glass plates, near together, with a wide channel on each side communicating with the tube above. The instrument was, however, found to be less sensitive in this form than when the half-cylinders were used.

The sensitiveness of the instrument could, to a certain extent, be altered by moving M and N (fig. 6) further apart, so that the phosphorus stream fell in a wider channel.

The divided tube was surrounded by another glass tube (G, fig. 5), which was about 10 centimetres longer. This formed the guard-tube, and was suspended from one of the axles of a clock (K, fig. 11), which made one revolution in about eight seconds.

By means of three levelling-screws the guard-tube was made to hang free of the inside tube, so that it did not touch it at any part of its revolution. Thus no heat due to friction was developed near the divided tube.

The phosphorus could not be placed at the top of the tube, as the falling column of oxide was found to go on one side of the partition, and its weight was sufficient to keep up a down-current of air on this side and an up-current on the other side, and so make the instrument unstable.

Inside the divided tube, and on one side of the partition, two fine platinum wires were stretched, reaching from the top

to the bottom. They were connected together at the top, and at the bottom were brought out and connected to two binding-screws fixed on the ring D (fig. 5). By means of this wire, whose resistance was measured, a known amount of heat could be developed in the tube by passing a current of known intensity. The current was, in all the experiments, supplied by a single Daniell cell, which contained in its circuit, beside the wire of the instrument, a resistance-box and a key.

The clock was kept working for about half an hour before the commencement of an experiment, in order to equalize the temperature within the tube ; and then a fresh piece of phosphorus was introduced. When the phosphorus index was quite steady, and approximately at the centre of the scale, the reading was taken (zero-reading), then resistance was unplugged in the box, and the current passed till the index had again come to rest. The current was then stopped, and another zero-reading taken.

In testing the different tubes the largest resistance which would give a readable deflexion was in each case ascertained. The resistance of the cell and the connecting-wires could be neglected in comparison with the external resistance.

In the different tubes the total heat developed was not the same when the same current was passed, as the wires were of different lengths. This, however, was not taken into account in comparing the tubes together, as for the measurement of the electromagnetic radiation it was necessary to get the greatest possible sensitiveness per centim. of the wire.

It is hardly necessary to give particulars of the different tubes experimented upon. It is sufficient to say that, while the length of the tube was of little consequence, it was found that a wide tube was much more sensitive than a narrow one. The results obtained in a particular case are given.

Tube No. 3 :—Length 82, diameter 5 centimetres. Resistance of wire 29 ohms ; outside resistance 500 ohms. Deflexion 1 millimetre.

To calculate the amount of heat corresponding to this deflexion, we have, taking the E.M.F. of a Daniell cell as 1 volt,

$$\text{Heat developed per sec.} = \frac{RC^2}{4\cdot2}$$

$$= \frac{29}{529^2} \times \frac{1}{4\cdot2} = \cdot000{,}024 \text{ calorie}$$

over the whole length of the tube, or ·000,000,3 calorie per centimetre of the tube.

While this very small degree of heating was within the range of experimental certainty so long as the clockwork was going, it was impossible to keep any index visible at all when the clock had stopped, even though several concentric screens were placed round the tube.

The apparatus in this form was subject to the great fault that the phosphorus refused to form the oxide at a temperature below 15° C., which prevented the instrument being used on many days.

With the view of getting over this difficulty with the phosphorus index, and if possible of obtaining greater sensitiveness, a form of index was adopted which was a modification of Dr. Joule's arrangement.

The tube was closed at each end, the partition reaching right up to the cork at the top and leaving a space of about fifteen centimetres at the bottom. Twelve centimetres below the top of the partition a hole was punched in the card. Into this hole a short cylinder of paper was glued. This is shown at A in figs. 8 & 9. A plane mirror, M, fitted into this tube, allowing about 1 millimetre clearance all round. It was fastened to a cross bar, at the other end of which a counterpoise (W) was fixed.

The mirror and counterpoise were suspended by a fine quartz fibre from a pin (E, fig. 8), which passed through the cork used to close the tube. When the mirror is at rest it almost completely fills up the hole in the partition, and forms a very delicate means of detecting any differences of pressure in the air at the two sides of the partition.

A small recess (B, fig. 9) was made in the partition for the counterpoise, and covered in so that it was not exposed to the current of air. The arrangement is shown in elevation in fig. 8, and in section through K L in fig. 9. Fig. 10 shows the mirror and counterpoise separately. A hole was ground in the tube immediately in front of the mirror, into which a lens of a metre focal length was cemented.

In this form of the instrument the guard-tube, if continuous, would have prevented the formation of a clear image. It was therefore necessary to divide it into two portions. Rings of mahogany (N, fig. 11) were cemented to the top of the lower portion and to the top and bottom of the upper. The two rings N_1 N_2 were connected together by three bolts, of such a length as to leave a space of about two centimetres between the rings. This break in the guard-tube came just on a level with the mirror, and thus allowed the beam of light to pass freely. The passage of the bolts before the mirror produced no inconvenient effect on the image formed on the

scale. The ends of the wire were brought out at the bottom of the tube, leaving about half an inch free. When using a continuous current, two brass clips (A, fig. 11) were placed on these ends so as to connect them to a pair of binding-screws. When using the oscillator these clips were turned down (as in the figure), so that the wire should not be connected with any body having capacity.

The following are the dimensions of this tube (No. 4):—

Length 126 centimetres, diameter 4·7 centimetres.

Length of wire 2 × 103 centimetres.

Resistance of wire 38 ohms.

Diameter of guard-tube 7 centimetres.

Diameter of mirror 1·2 centimetre.

Length of fibre 9 centimetres.

As shaking interfered with the working of the instrument, the experiments were performed in a vault, which, however, was by no means steady.

The following are the results obtained when testing the sensibility of the instrument (scale at 100 centimetres from mirror):—

Added Resistance.	Total Resistance.	Deflexion.
ohms.	ohms.	centimetres.
500	538	3·3
762	800	1·6

In the case of 800 ohms total resistance we have

$$\text{Heat developed in wire per sec.} = \frac{1}{800^2} \times \frac{38}{4{\cdot}2}$$

$$= {\cdot}000{,}014 \text{ calorie.}$$

This is equivalent to one calorie developed in 19 hrs. 42 min. Or we may say that one calorie per day developed by the whole wire could certainly be detected; that is, one calorie in 103 days per centimetre of tube.

The oscillator used to set up the electromagnetic radiation consisted of two hollow brass cylinders (D E, fig. 11), fixed to ebonite cross pieces (F, C), which could be placed at different heights in a wooden stand. Short brass cylinders, with well-rounded ends, fitted into the ends of D and E, and allowed the length and sparking-distance to be altered. These cylinders were connected by very fine wire with the terminals of the large Ruhmkorff's coil belonging to the Physical

Laboratory. The length of the oscillator was the same as that of either of the wires in the tube, and it was placed so as to be in the plane of the partition of the tube, at a distance of about 30 centimetres (fig. 11). The best length of spark was about half a centimetre.

At first, on separating the knobs of the oscillators, so that no spark passed, the instrument showed a large deflexion in the direction of cold. This was due to electrostatic attraction between the oscillator and the mirror. To prevent this action a piece of tin-foil (E F G H, fig. 8) was pasted round the tube at the level of the mirror, a hole being cut in it the size of the lens, which effectually put a stop to this action.

The instrument now indicated a considerable amount of heat developed in the wire whenever the coil was worked.

The effect of altering the capacity of the oscillator by adding pieces of tin-foil to the ends was tried, but with no beneficial result.

A wet duster was hung between the oscillator and the instrument for the purpose of seeing whether the radiation would pass through. The deflexion produced was only slightly less than when no duster was interposed.

In order to measure the heat developed by the induced currents in the wire, the deflexion produced when the coil was worked was noted; then a steady current was sent through the wire, and the resistance in the circuit altered till an equal deflexion was obtained. The readings obtained with the oscillator were somewhat varied, owing to small changes in the character of the sparks. Another difficulty was caused by the coil often refusing to work continuously for the time necessary to get a reading (about $1\frac{1}{2}$ minute), as the contact-breaker became burnt by the sparks.

The following are the deflexions obtained in centimetres :—

45 ; 44 ; 37 ; 36 ; 35·6 ; 36·9 ; 44·8 ;
45·5 ; 40·2 ; 40·2 ; 39.

Mean 40·4 *centim.*

One Daniell cell working through a total external resistance of 115 ohms gave the following deflexions :—

41·0 ; 40·0 ; 39·3 ; 40·0 ; 41·0.

Mean 40·3 *centim.*

We may therefore say that the heating-effect due to the oscillations (oscillator at 30 centim.) is equal to that pro-

duced by one Daniell cell when the external resistance is 115 ohms, and the working resistance 38 ohms.

Therefore the heat produced per sec.

$$= \frac{38}{115^2} \times \frac{1}{4 \cdot 2} \text{ calories},$$

$$= \cdot 000685 \text{ calorie};$$

or it would take 24 minutes 20 sec. to produce one calorie.

The steady E.M.F. between the terminals of the wire which produces the same effect as the oscillations is ·33 volt. Mr. Gregory gives ·5 volt as the equivalent E.M.F. in his experiments. Though the conditions were not sufficiently similar to make the numerical results strictly comparable, nevertheless the fact that the figures obtained are of the same order goes to show that the expansion observed by Mr. Gregory was a true expansion due to heat, and that his results were real.

In calculating from the heat developed the mean square of the current produced in the wire by the electrical oscillations, it is necessary to take into account the fact that these rapidly alternating currents are not uniformly diffused throughout the cross section of the wire, but only pass through a thin stratum at the surface. On this account the resistance which the wire offers to these rapidly alternating currents is greater than that which it offers to steady currents.

Lord Rayleigh * gives a formula for calculating the effective resistance of a wire of round section to an alternating current of given frequency. It is

$$R' = \sqrt{(\tfrac{1}{2} p l \mu R)},$$

where R′ is the effective resistance; R the resistance to steady currents in C.G.S. units; $p2\pi$ times the number of oscillations in one second; l the length of the wire; and μ the magnetic permeability of the substance of which the wire is composed.

In the following calculation one of the wires only is considered.

The length of the primary oscillator is 109 centimetres, and therefore the wave-length of the radiation given out is 218 centimetres. If n = number of oscillations per sec., then

$$n = \frac{v}{\lambda} = 1 \cdot 376 \times 10^8.$$

* Phil. Mag., May 1886, p. 388.

The length of the wire (l) is 103 centimetres, and its resistance 19 ohms $= 19 \times 10^9$ C.G.S. units.

In the case of platinum μ may be taken as unity.

From this it follows that

$$R' = 29 \text{ ohms},$$

and since H (half the heat developed in the two wires) $= \cdot 000342$ calorie per second

$$C^2 = \frac{JH}{R'}$$

$$= \cdot 000049.$$

Owing to the harmonic distribution of the current along the wire, in order to produce a given amount of heat in the whole wire, the strength of the current at the centre must be $\sqrt{2}$ times as great as that which would be necessary if the current were of uniform strength in all parts of the wire.

$\therefore$ the square root of the mean square of the current at the centre $= \cdot 01$ ampere.

While it is impossible from the heat found to form any conclusion as to how fast heat was being generated during each spark, or what fraction of the whole time the oscillations lasted, yet here, as in the former case, the final result depends on the mean square of the current. We found by the first method that the square root of the mean square was certainly not $\cdot 003$ ampere, if the theory was correct; while by the heat we find the square root of the mean square to be $\cdot 01$ ampere. The arrangements in the two cases were not strictly comparable, for in the first the oscillator was only 30 centimetres long, while in the second it was 109 centimetres, and because the distance of the primary from the secondaries was relatively greater in the first than in the second case. We intended to have made a second set of measures in which the suspended cranked oscillator should itself be in the tube of the convection-thermometer together with the fixed cranked oscillator. In this way the force, if any, between them could be observed and measured at the same time that the deflexion of the mirror due to the heat was read; then, by making contacts with the ends of the fixed cranked oscillator alone, and passing a current through it so as to produce the same deflexion, all the data would be obtained to tell for certain whether the absence of force, or, if force was observed, if the actual force was that which the provisional theory set out at the beginning of this paper indicated. The discrepancy of 3 : 10 in the present instance

cannot be taken as proving that the theory is wrong, and that the forces ought not to be observed, but it does clearly show that they must be excessively minute, and that, if they exist, it is only by great refinement that they can be made evident. No doubt, as Prof. Fitzgerald suggested, the use of concentrating cylindrical mirrors of proper form would greatly increase the sensitiveness of the whole apparatus.

We have been prevented from completing this work because the elementary laboratory was required, and it is impossible to carry on any really delicate research requiring uniform conditions and steadiness in so unsuitable a building as the Science Schools. We have therefore published our results in their present imperfect condition, partly because we believe that the methods employed may be useful to others, but chiefly because we hope that some physicist who has the advantage of having a steady underground room may be induced to make the experiments under more perfect conditions, and so carry the matter to a successful issue.

VI. *The Measurement of the Time of the Fall of Magnetization in a Magnetized Iron Cylinder. By* Frederick J. Smith, *M.A., Millard Lecturer on Mechanics and Physics, Trinity College, Oxford**.

WHILE working at the construction of electromagnetic styli, as used in the Tram Chronograph, described at p. 377, Phil. Mag. xxix., I wished to determine the conditions for producing a stylus with a small "latency." One of the principal things to be determined was the time of the fall of magnetization in different iron bars. As the determination of this period of magnetic change appears to be a subject of interest apart from the way in which it affects the action of styli, I beg respectfully to send you a brief account of the method by which I have arrived at certain results respecting it.

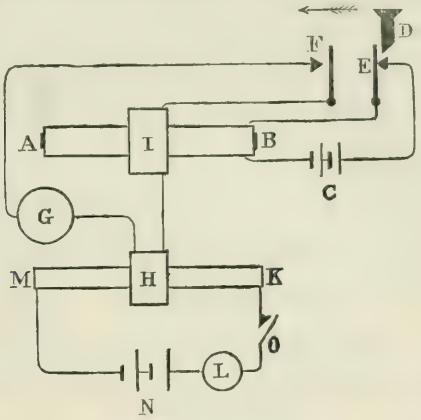
If an iron bar be magnetized by a current of electricity and the current be broken, the bar after a short time loses some of its magnetism. The time varies with the kind of iron used and the magnetizing force.

If the terminals of the coil conducting the magnetizing current could be quickly shifted from the battery to the terminals of a galvanometer, then a deflexion would be expected if the pole changing took place before the magnetization of

* Communicated by the Author.

the bar had quite run down. The experiment was tried, and always gave the expected result.

If, then, the exact time taken for pole changing could be measured, when the galvanometer just showed no sign of an induced current, this period of time would be that of the fall of magnetization of the bar. In practice such a change is just as well performed by having an arrangement, shown in the diagram, where an inductor-coil is suddenly connected to the galvanometer instead of the primary circuit, and the time is very gradually increased until no deflexion is produced.



A B is a long primary coil of known dimensions ; within this the iron cylinder to be tested is placed ; it is in circuit with a battery C, and a contact-piece E. I is an inductor-coil of known induction area, in circuit with the galvanometer G, the inductor H, and the contact-piece F.

The inductor H forms part of a system, consisting of a long helix M K, a battery N, an ampere-balance L, and a key O; by means of this system the value of the throw or deflexion of the galvanometer is determined in C.G.S. units, by the method of Sir W. Thomson.

The contact-pieces E and F differ from each other in their action. The circuit at E is broken when E is hit by a projection, D, attached to the carriage of the chronograph moving in the direction of the arrow, whereas the induction circuit is closed when D hits F. E is fixed, and F can be placed at any required distance from it. The distance E F determines the time which elapses between breaking the primary circuit and making the induction circuit. The primary circuit is always broken before the inductor-coil is connected to the

galvanometer circuit; so that the induction due to the iron cylinder, apart from that due to the coil, is measured at any time after the breaking of the primary circuit. The time of traverse of the distance E F is determined from the trace of the chronograph up to the $\frac{1}{20,000}$ second.

All the induction apparatus is placed at a great distance from the galvanometer, so that it is in no way affected by it. After the value of the deflexion of the galvanometer has been obtained, the ampere-balance is used in the circuit of the coil A B for determining the field due to the magnetizing coil. A series of determinations of this *After-Induction* are now being made in the Laboratory, but as the necessary reductions will take some time to finish they cannot be sent with this communication. In one experiment on a certain iron bar the After-Induction took place up to 0·015 second.

December 13, 1890.

VII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xxx. p. 281.]

November 12, 1890.—Dr. A. Geikie, F.R.S., President, in the Chair.

THE following communications were read:—

1. "On the Porphyritic Rocks of the Island of Jersey." By Prof. A. De Lapparent, Foreign Correspondent of the Society.

The author had some years ago described as Permian a series of porphyritic rocks, of which specimens had been sent to him from Jersey. He had since been led to believe that this view of their age, arrived at from what he knew of similar rocks in France, was erroneous, and in a recent visit to the island had satisfied himself that the English observers who had assigned to these rocks a much higher antiquity were in the right. He now found that the igneous rocks in question underlie the Rozel conglomerate, which must be placed at the very base of the Silurian formations. He reserved his detailed statement for a communication to the Geological Society of France; his present object being to do justice to English geologists, whose views he had formerly opposed.

2. "On a new Species of *Trionyx* from the Miocene of Malta, and a Chelonian Scapula from the London Clay." By R. Lydekker, Esq., B.A., F.G.S.

3. "Notes on Specimens collected by W. Gowland, Esq., F.C.S., in the Korea." By Thomas H. Holland, Esq., of the Geological Survey of India, late Berkeley Fellow of the Owens College.

The southern half of Korea traversed by Mr. Gowland is of a hilly character. The rocks forming the hills are chiefly crystalline schists—gneisses with graphite, garnet, dichroite, and fluor occurring in considerable abundance, and the whole group is probably part of the great Archæan mass of North-east China. The author describes these metamorphic rocks in detail.

Stratified rocks, probably of Carboniferous age, lie unconformably upon the schists in the south-eastern part of the peninsula, and petrographical notes of these are given in the paper. Through the crystalline schists and stratified rocks various igneous rocks have been erupted as dykes or in large masses. Amongst these the most conspicuous rock is granite. Biotite- and muscovite-granite are most widely distributed, and in places are cut by dykes of eurite and veins of quartz and pegmatite. The more basic class of rocks is represented by diorites, propylites, andesites, basalts, dolerites, and gabbros. Interesting cases of the gradual passage between the so-called intermediate and basic rocks are found, and various stages in the devitrification and decomposition of andesitic lavas represented. These are described in detail by the author, and compared with similar cases in other regions; and full descriptions of the intrusive rocks are furnished.

There are now no active volcanoes; and there is a notable lack of mineral wealth in the southern part of the Korea.

4. "Further Notes on the Stratigraphy of the Bagshot Beds of the London Basin (north side)." By the Rev. A. Irving, D.Sc., F.G.S.

1. The author brings forward new evidence from well-sections, clay-pits recently opened, and excavations, confirming the reading of the country between Wellington-College and Wokingham Stations on the S.E. Railway, as put forward by him in 1887 (Q. J. G. S. vol. xliii. and figure 1 of the paper). We have now actual data for the gradients of the clay-beds, and the thinning-out of both the Lower (fluviatile) Sands and of the Middle green-earth series; the latter, when taken into account, bringing the clays in the Wokingham outlier into stratigraphical alignment with the basal clays of the Middle Group. Certain clays at California are also shown to be in alignment with these; and a sketch-section from Ambarrow to Barkham Hill shows the relative gradients of certain horizons to be such as to justify the relegation of the Pebble-bed there to the base of the Upper Sands; while a microscopical examination of the sands above it brings out the lithological identity of these and of the sands capping Farley Hill with the basal beds of the Upper Sands at Wellington College and on Finchampstead Ridges. The accidental occurrence

of thin seams of pipe-clay is rejected as a test of horizons, as affording only ambiguous evidence.

2. A similar succession is shown in a section drawn from Wellington College Well through the sand-pit at the brick-yards by Ninemile Ride (base of the Middle Clays exposed), Easthampstead Church Hill (with more recent data), and Bill Hill (Easthampstead), to the S.W. Railway at Bracknell, bringing the higher beds of those two hills into the horizon of the Upper Sands. Further notes are also added to those of the author's 1888 paper (Q. J. G. S. vol. xliv.) on the Ascot Hills, Englefield Green, and Windsor Park, where the transgressive relation of the Bagshot Beds to the London Clay is maintained.

3. In conclusion, the author points out that the new well-sections confirm the trustworthiness of that at Wellington College as a vertical datum-line; he criticizes the views of previous writers and maintains that, with the aid of Lieut. Lyons' recently published contour-map, we can now discriminate between the effects of contemporaneous and post-Eocene earth-movements in the area: and that the physical history of the Bagshot Beds, which he has himself propounded, is substantiated by the stratigraphical evidence.

November 26.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "Account of an Experimental Investigation of the Law that Limits the Action of Flowing Streams." By R. D. Oldham, Esq., A.R.S.M., F.G.S., Deputy Superintendent of the Geological Survey of India.

The author brings forward evidence derived from experiments in support of the views expressed in a paper submitted to the Society in 1888. His apparatus consisted of a sloping trough, through which various amounts of water containing definite percentages of sand could be sent. The lower end of the trough issued on to a semicircular platform.

In three experiments with the trough at a slope of 1 in 20, and with the same work to be done in each case, the resulting slopes after sand had accumulated in the trough were as follows:—With one part of sand to 42 of water, a slope of 1 in 40; with 1 of sand to 28 of water, 1 in 20; and with 1 of sand to 14 of water, 1 in 13·3. These slopes were obtained when a condition of equilibrium had been maintained so that the water was just able to transport its burden. By increasing the supply of water from 14 : 1 to 42 . 1, the original slope was eventually obtained.

On the fan formed on the horizontal platform variations in the water-supply did not produce nearly so marked an effect as in the confined channel, and the slope varied considerably in different directions.

After a time a channel was cut back into the fan, and its sand swept forward and deposited as a secondary fan in front of the first:

and as this grew, it cut back into the reach above, and this in turn cut back towards the head of the fans, and sometimes into the trough. In some cases other secondary fans were formed on the margin of the main fan, but the apparatus was not large enough for further formations. The general slope of the fans, both primary and secondary, was ·06, and that of the reach only ·04, while at the head of the reach, where it was cutting back into the face above, there was a gradient of ·08.

The general tendency of the experiments supports not only the specific conclusions as to the normal form and behaviour of a river which has attained a state of equilibrium, but to a greater degree the fundamental assumption that a river will adapt its channel to such a slope and form as will enable it to just transport a solid burden cast upon it.

2. "On the Rocks of North Devon." By Henry Hicks, M.D., F.R.S., Sec.G.S.

During a recent visit to North Devon the author obtained evidence which has led him to believe that far too little importance has hitherto been assigned to the results of movements in the Earth's crust as affecting the succession of the rocks in that area. The supposed continuous upward succession from the rocks on the shore of the Bristol Channel to those in the neighbourhood of Barnstaple, including, according to some authors, no less than ten groups, and classed into three divisions under the names Lower, Middle, and Upper Devonian, is, the author believes, an erroneous interpretation. The beds, he says, have been greatly plicated and faulted, and consequently several times repeated, and instead of being one continuous series, they occur folded in more or less broken troughs. In the Morte Slates, previously considered unfossiliferous, the author found a *Lingula*, and he believes that these slates are the oldest rocks in the area, and formed the floor upon which the Devonian Rocks were deposited unconformably. As the result of movements in the Earth's crust, the Morte Slates have been brought to the surface and thrust over much newer rocks, producing a deceptive appearance of overlying the latter conformably. The Morte Slates mark the dividing line between the two main troughs. On the north side in ascending order are the Hangman (or Lynton), Combe Martin Bay, and Ilfracombe Beds, and on the south side the Pickwell Down, Baggy Point, and Pilton Beds. Those on the south side of the Morte Slates are, the author believes, a repetition of the beds on the north side. The palæontological evidence is not antagonistic to this view, for an analysis of the Brachiopoda, the only group of fossils in the beds on the south side, which hitherto have been systematically examined, shows that of the twenty species mentioned by Mr. Davidson and others as occurring in the Pickwell Down, Baggy Point, and Pilton Beds (the so-called Upper Devonian Rocks), no less than thirteen have already been found in the Middle or Lower Devonian rocks on the north side of the Morte Slates. Four others are recognized

Middle Devonian species in other areas; and the three remaining are either doubtful species or ones which have a great vertical range. These facts show that the so-called Upper Devonian Rocks in this area do not contain a distinguishing fauna of any importance; and the stratigraphical evidence is opposed to the view that they are a series of rocks distinct from those on the north side of the Morte Slates, which have been classed as Middle and Lower Devonian.

December 10.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On some Water-worn and Pebble-worn Stones taken from the Apron of the Severn Commissioners' Weir erected across the River at Holt Fleet about 8 miles above Worcester." By Henry John Marten, Esq., M.Inst.C.E., F.G.S., &c., Engineer to the Severn Commissioners.

The Weir referred to in the paper was built in 1844 of soft red sandstone, and some of the stones composing the apron of the Weir showing signs of decay were removed in 1887. The average quantity of water passing over each square foot of the stones composing the apron has been estimated at about 2000 gallons per minute. A large proportion of the stones had been drilled through and through by the action of the current upon small pebbles lodged in hollows or between the joints of the stone; and the author estimates that as a result of 43 years of erosion, six of the stones of the apron, which may be taken as a sample, had lost the following amounts respectively:—45, 60, 48, 50, 37, and 58 per cent.

2. "On the Physical Geology of Tennessee and adjoining Districts in the United States of America." By Prof. Edward Hull, M.A., LL.D., F.R.S., F.G.S., late Director of the Geological Survey of Ireland.

The area described in the paper is occupied by the Unaka or Blue Ridge, which may be regarded as one of the parallel ridges of the Alleghanies, and the prolongation of Prof. J. D. Dana's "Archæan Protaxis." It runs in a general south-westerly direction, and attains an elevation of 6760 feet. At its base, and to the north-west of it, is the Valley of East Tennessee, about 40 miles wide, and furrowed by north-east and south-west ridges and depressions, parallel to the strike of the Cambrian and Silurian beds. Through this runs the Tennessee River, which, instead of running south to the Gulf of Mexico, turns to the north-west, some distance below Chattanooga, and cuts through the Cumberland table-land, a prolongation of the Appalachian mountains, and flows into the Ohio river.

The Cumberland table-land has an average height of 2000 feet above the sea, and 1350 feet above the Tennessee River at Chattanooga. It consists of a synclinal of Carboniferous rocks resting conformably upon the Devonian beds, and is bounded along the East Tennessee Valley by a curved escarpment; a similar though more indented escarpment forming its north-western margin, and separating

it from the Silurian plain of Nashville. The table-land is about 40 miles wide, and is intersected by the valley of the Sequachee River, running in a north-easterly direction along a subsidiary anticline from near Jasper for a distance of sixty miles.

From the base of the Cambrian beds, the whole Lower and Upper Palæozoic formations succeed each other in apparently conformable sequence, except at the junction of the Upper and Lower Silurian series, where a probable discordance occurs. The prolonged period of subsidence and deposition at length gave way to elevation; acting with the greatest effect along the Alleghanies. Under these circumstances, denudation preceded most rapidly along the tract bordering the Protaxis, whilst the synclines were protected from erosion to a greater degree; and as the elevatory movement was more rapid along the Unaka range, the flow of the streams was generally westward. At a later period the Cumberland plateau began to be formed by backward erosion of the strata in the direction of the dip; so that it owes its development to the erosion of the Tennessee and Clinch rivers on the one hand, and to the Cumberland river on the other. Where the Tennessee River flows in a north-westerly direction through the Cumberland plateau, the divide between it and the Gulf of Mexico is only 280 feet above the river-bed, whilst the table-land is 1400–1500 feet above. The author infers, therefore, that when the river began to erode its channel the plateau was relatively lower than the tract to the south of the present course of the stream, but that by denudation the relations have been reversed, whilst the river has never left its originally selected course.

The author compares the state of things with that which must have occurred in the case of the northerly rivers running from the centre of the Wealden axis; but mentions that Prof. Safford and Mr. J. Leslie account for the Cumberland plateau by faulting, though he thinks that the well-defined escarpment along the valley of East Tennessee seems to show that this cause is insufficient.

In conclusion, he believes that the denudation was accelerated during the pluvial or "Champlain" period, and calls attention to the "Columbia formation" of the east side of the Alleghanies, and to the deposit of red loam by which the surface of the country of the valleys of the Tennessee and Sequachee is overspread, and which is probably referable to a similar stage.

3. "On certain Ornithosaurian and Dinosaurian Remains." By R. Lydekker, Esq., B.A., F.G.S.

VIII. *Intelligence and Miscellaneous Articles.*

EXPERIMENTAL INVESTIGATIONS ON THOMSON'S LAW OF WAVE-MOTION ON WATER. BY O. RIESS.

THE influence of surface-tension on the wave-motion of water was, as is well known, first theoretically investigated by Sir W.

Thomson, and by Kolaček, and expressed by the formula

$$v^2 = n^2\lambda^2 = g\left(\frac{\lambda}{2\pi} + \frac{2\pi}{\lambda}\mathrm{T}\right), \text{ and } v^2 = g\left(\frac{\lambda}{2\pi} + \frac{2\pi}{\lambda^2}\mathrm{T}\right).$$

The velocity of propagation v is thus a function of two forces which are independent of each other—g (gravity) and T (surface-tension). On the other hand, considered as a function of λ, it has a minimum, namely 2·311 centim. for the wave-length $\lambda = 1{\cdot}709$ centim.; so that from this there results a natural division of waves into two classes—ripples and large waves. Although observations on ripples have been made by Thomson, Matthiesen, Lord Rayleigh, Arendts, and others, these observations are wanting in the requisite accuracy, and accordingly the author has carried out systematic observations by various methods which control each other. In the first method, tuning-forks were used to produce the waves; in the second, the simultaneous vibration of the armatures of two electromagnets; and finally in the third, which was made on a large scale in the Rostock filtering-basins, small plates which were fixed to rods at the level of the water. Stationary waves were always used, as these are more favourable for observation and for calculation. Reference must be made to the original for the observation of the numbers of vibrations and the wave-lengths in the individual cases, and for the manner in which the numerous difficulties were overcome. As the results of the various methods are essentially the same, it will be sufficient here to give a summary of that of the first. Five different tuning-forks gave the following results:—

n.	λ, in centim.		$\Delta\lambda$.	v, calc. in centim.		Mean of one observation	Error of the result.
	Calc.	Obs.		Thomson.	Obs.		
8·415	2·947	2·764	0·183	24·80	23·26	0·029	0·004
16·215	1·435	1·321	0·114	23·27	21·42	0·009	0·001
36·677	0·739	0·675	0·064	27·10	24·76	0·020	0·009
37·140	0·732	0·670	0·062	27·19	24·88	0·011	0·008
64·635	0·493	0·450	0·043	31·87	29·09	0·005	0·000

The calculation of Thomson's results was made by putting

$$\frac{981\cdot4}{6\pi n^2}\sqrt{\frac{1}{3\pi^2\mathrm{T}}} = \tan\alpha, \quad \sqrt[3]{\tan\frac{\alpha}{2}} = \tan\rho, \quad \lambda = \sqrt{3\pi^2\mathrm{T}}\tan 2\beta;$$

and from this λ, and therefore v, was calculated. It will be seen that the experiment agrees sufficiently well with the theory as regards the position of the minimum of v, and of the general course of the values of λ and v; on the other hand, all the observed values are considerably smaller than the calculated ones. In order to follow this more minutely, measurements were made at various

temperatures (the above hold for 20°), and the following result was obtained :—

0°.		20°.		40°.		60°.		80°.	
n.	λ.	*n*.	λ.	*n*.	λ.	*n*.	λ.	*n*.	λ.
8·418	2·848	8·415	2·764	8·411	2·701	8·405	2·656	8·394	2·628
16·224	1·384	16·215	1·328						
36·695	0·715	36·677	0·675	36·653	0·645	36·617	0·623	36·551	0·608
37·160	0·709	37·140	0·670						
64·668	0·477	64·635	0·450	64·591	0·430	64·525	0·415	64·404	0·404

It is apparent from this that the want of agreement between theory and experiment is to be sought in the dependence of surface-tension on temperature on the one hand, and on the wave-length on the other. If this dependence is eliminated, we get the following values :—

λ.	T_0.	λ.	T_{20}.	λ.	T_{40}.	λ.	T_{60}.	λ.	T_{80}.
2·848	0·0600	2·764	0·0490	2·701	0·0413	2·656	0·0360	2·628	0·0324
0·715	0·0669	0·675	0·0557	0·645	0·0479	0·623	0·0429	0·608	0·0393
0·477	0·0678	0·450	0·0566	0·430	0·0491	0·415	0·0439	0·404	0·0402

From this we obtain for 0° the formula

$$v^2 = g\left(\frac{\lambda}{2\pi} + \frac{2\pi}{\lambda}(0{\cdot}070 - 0{\cdot}0_4411\,\lambda^{0{\cdot}84})\right),$$

and for various temperatures the formula

$$v^2 = g\left(\frac{\lambda}{2\pi} + \frac{2\pi}{\lambda}(T_0 - 0{\cdot}0_3591\,t + 0{\cdot}0_5311\,t^2)\right),$$

in which T_0 is the expression within brackets of the first formula. This latter value vanishes for $\lambda = 28$ centim. ; according to Thomson the influence of surface-tension on this wave-length would still be $T_0 = 0{\cdot}1$ centim., that is about $\frac{1}{3}$ per cent. For an infinitely small λ $T_0 = 0{\cdot}070$, which agrees sufficiently with the values ordinarily assumed. It may be observed that with other methods the number of vibrations went down to 2·67 and the wave-lengths rose to 21·915, while the T_0 sank to 0·0130, and that nevertheless the above two formulæ for v^2 agreed very well. The actual state of the case lies between Kolaček's formula and that of Thomson for $\lambda = 1{\cdot}672$: for instance, according to Thomson $n = 13{\cdot}83$; according to Kolaček, $n = 12{\cdot}33$; experiment, $n = 13{\cdot}33$.

Hence T is proportional neither to λ nor to λ^2.—Exner's *Repertorium der Physik*, xxvi. p. 102 (1890); *Beiblätter der Physik*, xiv. p. 938.

ON THE CONDENSATION OF AQUEOUS VAPOUR IN CAPILLARY SPACES. BY G. VAN DER MENSBRUGGHE.

The author propounds the task of furnishing an exact experimental proof of Thomson's theory, that the maximum pressure of aqueous vapour for a given temperature is smaller for a concave surface than for a plane one, and continually decreases with increasing concavity. In the first part of the present research a number of facts are collected which serve as examples for the condensation of aqueous vapour in capillary spaces. Mention is made of the microscopic capillary slits in organic hygroscopic structures, the deposition of ice-flowers on the dusty parts of our window-panes, the phenomenon that particles of iron rust most when they appear protected by materials, such as cloths, dry wood, and the like, which are in contact with them.

In reference also to Aitken's experiments on the fog-producing action of suspended particles of dust, the author urges as the explanation the irregular shape and the ultra-capillary cracks of the individual particles. The author observes incidentally, that the rapid rotting of fabrics, such as tulle, which are often coated with aqueous vapour even in air which is far from its point of saturation, may be explained by thermoelectric currents which are formed on moistening and on drying (*Bull. Ac. Belg.* [2] vol. xli. p. 769, 1876). The durability of the clothing with which Egyptian mummies are wrapped depends on the filling of the capillary cracks with wax. The author strongly recommends that for the preservation of oil-paintings they should be varnished on the back.—*Bull. Ac. Belg.* [3] vol. xix. p. 101 (1890); *Beiblätter der Physik*, No. 11, 1890.

ON ELECTRICAL CONVECTION. BY A. RIGHI.

In this note the author describes new experiments, which taken in conjunction with those he has previously published appear to him to establish:—

That in all cases in which there is an escape of electricity either by a point, or by an incandescent body, or by a metal exposed to ultra-violet radiations, the phenomenon is due to convection; and that the particles in movement follow sensibly the lines of force of the field in which they move. In more or less rarefied air the trajectories seem to diverge more and more from the lines of force; and in the case of an extreme degree of rarefaction they should become almost rectilinear, as appears to be the case with the particles of radiant matter in Crookes's tubes.

The author proposes to make experiments to see if this gradual

passage from one to the other of the two extreme forms of the phenomenon does really take place.—*Rendiconti della Reale Accademia dei Lincei*, vol. iv. pp. 151, 189; *Journal de Physique*, Nov. 1890.

ON THE PHOTOGRAPHIC ACTION OF ELECTROMAGNETIC WAVES.

BY FRANZ VON DOBRZYNSKI.

For several months I have been engaged in investigating the photographic action of electromagnetic waves. On May 1 I observed an indication of this action, and on July 9 the action itself.

The electromagnetic waves were obtained by the method of Hertz. They acted on dry bromide of silver and gelatine 'Nys' plates procured from Geissler in Bonn.

The plane of the plates either included the axis of the vibrator or was at right angles to it. The exposure was three hours. No sensitization of the plates was made. The development and fixation took place in the ordinary manner by ferric oxalate and hyposulphite.

The action was visible after development and fixation by the appearance of alternating bright and dark bands across the direction of vibration of the waves, or by the appearance of dark bands in the direction of the vibration. Both kinds of bands could occasionally be observed together.

In many experiments the plates were covered with tinfoil. Portions of the coating of the tinfoil were cut away. The tinfoil did not prevent the formation of bands. This points to the fact that the chemical action which here comes into play is not a primary one.

The cross bands suggested stationary vibrations. They might be due to reflexion from the sides of the wooden box, by which the plates were protected from the influence of extraneous rays; but they might also owe their origin to reflexion from the side of the room*.

The only experiment which could be made with a reflecting metal ball was not in disagreement with this view; the cross bands were now more distinct and regular.

If this view is correct, it may be concluded that waves of from 0·6 to 20 centim. are effective.

The complete description of the mode of experimenting I will defer until I communicate further investigations in this direction. —*Wiener Berichte*, October 9, 1890.

* The plates often contained two systems of cross bands. These would represent different waves which the vibrator emits in the sense of the discovery of Sarasin and De la Rive, and in that of the view stated above.

QUANTITATIVE PHOTOGRAPHIC INVESTIGATION OF ELECTRICAL OSCILLATIONS. BY J. MIESLER.

The object of the present research is to show the agreement between the times of oscillation of the Leyden Jar as found photographically, with the times calculated from the measured capacities and the coefficient of self-induction of the jars and the circuit; there being as yet no long comparative series of numbers. The photographs were taken by means of a rotating plane mirror and an object-glass. The times of rotation were then deduced from the dimensions of the photographs.

The coefficient of self-induction of the wire used in each case was determined by a null method by comparison with a condenser divided into thousandths of a microfarad. The capacities of the Leyden jars used in the separate observations were compared with this condenser by means of an electrometer. The time of vibration was determined from these two last series of data by means of the formula

$$T = \pi \sqrt{CL},$$

and compared with those deduced from the photographs, and it was found that there was a very close agreement. The thickness of the wires was always 0·8 mm., so that the above formula holds strictly for thin wires.—*Wiener Berichte*, July 1890; *Beiblätter der Physik*, No. 11, 1890.

ON THE SMALLEST PERCEPTIBLE VISUAL ANGLE IN THE VARIOUS PARTS OF THE SPECTRUM. BY W. UHTHOFF.

A spectrum more than 20 cm. in length was projected from zirconium light, through a large prism filled with cinnamic ether, and corresponding lenses, from which in seven places a portion 3 mm. in diameter could be cut off by a sliding metal screen. If the eye looked through the aperture of this screen, it saw the nearest face of the prism illuminated by the corresponding homogeneous colour. A wire grating could be moved backwards and forwards in the path of the rays. The wires were at a distance in the mean of 0·0926 mm. apart, and the intervals were exactly equal to the thickness of the wire. From the distance from the eye at which the grating had to be placed, so that the wires were just invisible, the sharpness of vision could be deduced for the various colours. This was almost the same for all colours; in the case of the author the smallest visual angle under which the eye could distinguish the object (the breadth of a wire and the space taken together) was 55·2, and for A. König 65·6 seconds, from which it is inferred that the diameter of the elements in the retina concerned in this is 0·002 to 0·004 mm.—*Zeitschrift für Psychol. und Physiologie*, i. p. 155; *Beiblätter der Physik*, No. 11, 1890.

Figs. 5 to 11
Scale $\frac{1}{3}$

Fig. 9.

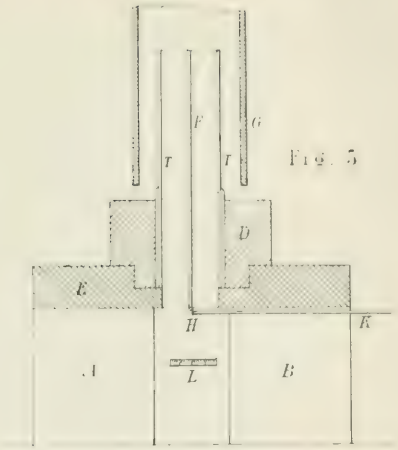


Fig. 5

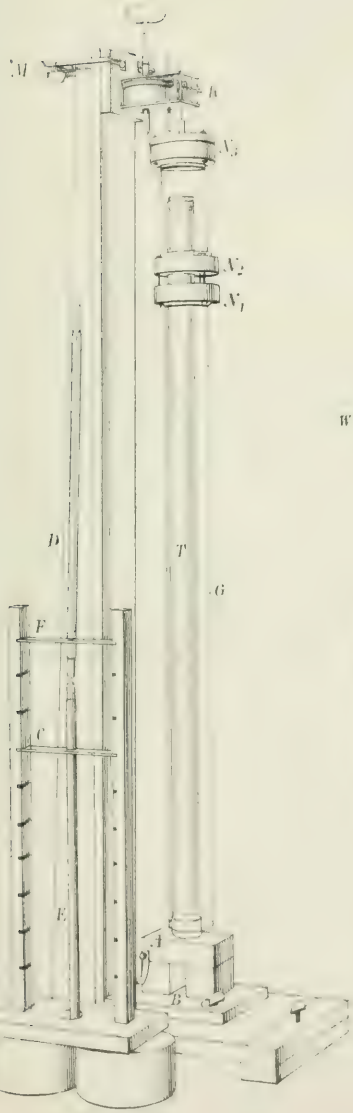


Fig. 11.

Fig. 10.

Fig. 7.

Fig. 8.

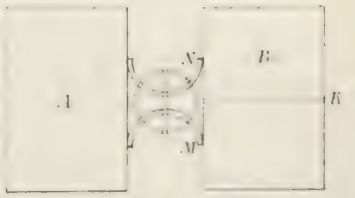


Fig. 6

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PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

FEBRUARY 1891.

IX. *The Elementary Treatment of Problems on the Diffraction of Light.* By ARTHUR SCHUSTER, *F.R.S.**

THE complete investigation of problems relating to the diffraction of light involves the discussion of certain definite integrals which often cannot be introduced at the stage at which students begin to learn the important subject of Physical Optics. Most of our text-books give therefore a more elementary treatment of the question in which the wave-front is broken up into elements or zones, the effects of which are added up algebraically. This elementary treatment suffers from a very serious defect, if anything more than a very general explanation is aimed at, for the considerable difference of phase in the resultant effect of the first and subsequent elements is altogether neglected. Prof. Mascart, in his excellent book on Optics, obtains numerical results from such elementary considerations; but he takes without justification the phase of the central element to be the same as that of the others, and his treatment is therefore open to the objection which I have indicated. It is true that the intensities of the diffraction-bands at the edge of shadows, as calculated in the elementary way, do not differ much from those obtained by a more rigorous analysis; but the position of the bands is not correctly given, and the question of the resultant phase is altogether left out of account. Even to those who can follow the complete investigation by means of Fresnel's integrals, the method of breaking up the wave-front into

* Communicated by the Author.

separate parts is very instructive; and I hope therefore that the following way of treating the subject, which seems to me to be free from objection, and gives numerical results practically identical with those obtained by Fresnel, will be found to be of use.

For the sake of subsequent reference it is necessary to say a few words on the division of a wave-front into circular zones. I shall only consider plane waves, but the results may easily be extended to other cases.

In order to calculate the amplitude produced at a point P by a plane wave-front at a distance p from it, circles are drawn such that their distance from P is $p+\frac{n\lambda}{2}$, n being an integer. The plane is thus divided into so-called Huyghens zones, the areas of which are equal as long as $n\lambda$ is small compared to p. The effect of a single zone can be obtained by subdividing it into narrower rings of equal areas, when it will be found that the phase of vibration at P due to such elementary rings will vary uniformly over two right angles. The phase of the resultant vibration will therefore be halfway between that due to the extreme portions, and the amplitude is obtained by reducing, in the ratio of $\pi : 2$, the amplitude calculated on the assumption that the phase due to each part of the zone is the same (Lord Rayleigh, Phil. Mag. xlvii. 1874). This is true also for the first circular area. The effect of two successive zones is therefore strictly opposite in direction, and we can calculate the whole effect by means of a series

$$m_1-m_2+m_3-m_4+\dots .$$

The sum of this series, as may be shown, is $\frac{m_1}{2}$, and the phase of the resultant vibration will be one right angle behind that due to the central point.

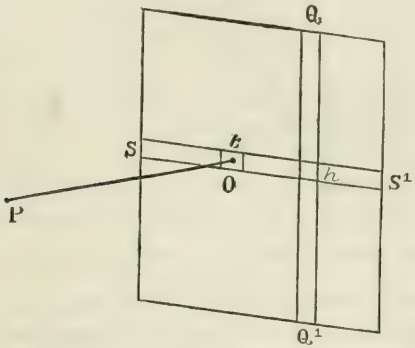
To calculate m_1, let the amplitude of vibration be unity. If a small surface s, taken out of the wave-front, will produce an amplitude κs at P, the central area will produce an amplitude $\frac{2\kappa}{\pi}.\pi r^2$, where r is the radius; the factor $2/\pi$ being applied, as just explained, because the phases due to different parts of the central area range over two right angles. As r^2 is equal to $p\lambda$, the effect of the first zone, as regards amplitude, will be $2\kappa p\lambda$, and the whole wave-front will cause an amplitude equal to half this value, which must obviously be equal to unity, because a plane wave does not alter in amplitude during its propagation. It follows that $\kappa=1/p\lambda$; and hence that if s be a small surface at a distance p from a

point P the amplitude due to s at P is $\frac{sa}{p\lambda}$, where a is the amplitude at s; and this agrees with the more complete result obtained by Stokes for the case where the angle between the normal to s and the radius vector to P is so small that its square may be neglected.

We are now prepared to subdivide the wave-front into rectangular elements.

From P (fig. 1) draw a perpendicular P O to the wave-

Fig. 1.

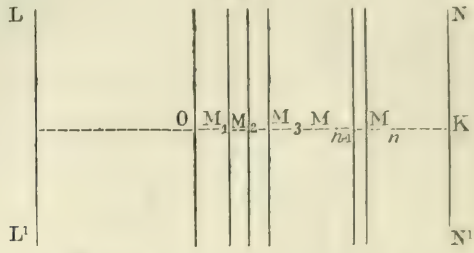


front and consider a central strip S S¹, of width h, subdivided into smaller areas, the middle one having a length t. The effect of this area at P, as regards amplitude, is $\frac{th}{p\lambda}$, the amplitude of the wave being unity, and t and h being small compared to a wave-length. The amplitude of the strip S S¹ can be expressed in the form $\frac{\kappa h}{p\lambda}$, where κ is a quantity to be determined. If the effect due to S S¹ is known, that due to the whole wave-front may be calculated; for on any portion having a length t' a rectangular strip Q Q¹ could be erected, the effect of which could be determined by applying the same factor which converts the effect of the central element at O into the strip S S¹; that is to say, if $\frac{\kappa h}{p\lambda}$ is the effect of S S¹, $\frac{\kappa^2}{p\lambda}$ will be the effect of the complete wave; and as this is unity, it follows that $\kappa = \sqrt{p\lambda}$: hence the effect due to a strip of width h and of indefinite length will be $\frac{h}{\sqrt{p\lambda}}$. A similar reasoning shows that the phase due to such a strip differs by half a right angle from the phase due to the central portion at O.

In order to find the effect at P of a wave-front bounded by

two straight lines, L L^1, N N^1 (fig. 2), draw the perpendicular P O, and divide the wave into rectangular strips such that the

Fig. 2.



resultant phase of two successive strips shall be opposite, the phase of alternate strips agreeing with that of the whole effect at P. It is obvious how to find the positions of the points M_n, M_{n-1} when these are not close up to O ; for as the whole resultant has a phase which corresponds to a distance $PO+\frac{\lambda}{8}$, and as, except for the central strips, the resultant phase at P will be very nearly that corresponding to the arithmetical mean of the extreme distances, we shall satisfy the condition by making

$$PM_{n-1}=p+\frac{4n-5}{8}\lambda,$$

$$PM_n= p+\frac{4n-1}{8}\lambda.$$

We shall assume that this is allowable until we come to the central strip ; so that $PM_1=p+\frac{3}{8}\lambda$. This division differs from that usually adopted, and herein consists the great advantage of the method of reduction which I propose.

We divide, then, the central line O K into elements such that

$$PM_1=PO+\frac{3\lambda}{8},$$

$$PM_2=PM_1+\frac{\lambda}{2},$$

$$PM_3=PM_2+\frac{\lambda}{2}.$$

It has already been shown that, after the first few elements, the resultant vibration due to the elementary strips is that corresponding to a distance $p+\frac{\lambda}{8}$. If this is true for all

elements down to the first, it must also be true for the first, because the whole resultant shows a difference of phase corresponding to that distance. In the usual way of treating the subject, PM_1 is taken to be $PO+\frac{\lambda}{2}$; the result being that the first element produces a phase differing considerably from that of the succeeding ones: by reducing the width of the first strip we make the difference of phase nearly equal to that of the others.

The following Table shows the phases of the vibration at P due to successive strips, as calculated by means of Fresnel's integral, both for the case in which the old division is taken and the one here suggested.

	Usual division into strips.	Suggested division into strips.
Resultant Phase due to first strip	53° 20′	42° 40′
,, ,, second strip...	180°+80° 18′	180°+38° 15′
,, ,, third strip ...	86° 15′	44° 20′
⋮ ⋮ ⋮		
Converging towards	90°	45°
and	180°+90°	180°+45°

If, then, the usual division into strips is adopted, and the amplitude due to all the strips is added up algebraically, as has been done by Mascart and others, a difference of phase of 37 degrees is treated as non-existent. On the other hand, in the division which I suggest, all phases are nearly equal. The second strip shows the greatest difference of phase, but as the cosine of 7° differs by less than one per cent. from unity the results of the calculation will be sufficiently accurate.

We shall apply this new division into strips to calculate the position and intensity of diffraction-fringes at the edge of shadows cast by straight boundaries. It will be necessary in the first place to calculate the amplitude produced by each strip separately. Assuming, as before, that the phase of vibration at P produced by the subdivisions of each strip after the two central ones, range uniformly over two right angles, the amplitude produced at P will be $\frac{2}{\pi}\cdot\frac{h}{\sqrt{\rho\lambda}}$, where h is the width of the strip. Neglecting squares of λ, we find that the width M_1M_2 of the second strip is

$\sqrt{p\lambda}.(\sqrt{7}-\sqrt{3})/2$, that of the third $\sqrt{p\lambda}.(\sqrt{11}-\sqrt{7})/2$, and so on.

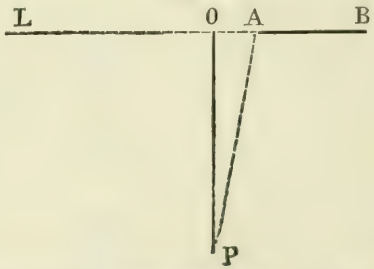
The total effect of all the strips on one side of O after the first will therefore be

$$\frac{1}{\pi}[(\sqrt{7}-\sqrt{3})-(\sqrt{11}-\sqrt{7})+(\sqrt{15}-\sqrt{11})-\dots].$$

The expression in square brackets converges towards the limit ·5420, and hence the effect of a wave of indefinite extent from M_1 outwards will be $\cdot 5420/\pi = \cdot 1725$.

From this we may calculate the effect of the first strip OM_1, for each half of the wave-front on either side of O must produce an amplitude of one half. As the effect of the second strip counteracts that of the first, the latter must cause an amplitude at P, which is numerically represented by ·6725, the amplitude of vibration in the original wave being taken as unity. It is now easy to calculate the amplitude of successive diffraction-bands (fig. 3). P represents the point at

Fig. 3.



which the amplitude is to be calculated, L A is a section of the plane wave-front, and A B a section of the screen which casts the shadow. The intensity at P will then be a maximum, to the degree of accuracy of which our method is capable, if the screen cuts off all strips on one side except the first, for in that case $PA = PO + \frac{3}{8}\lambda$, and the phase due to OA is the same as that due to a distance $PO + \frac{1}{8}\lambda$. If the screen were removed further away from O it would expose parts of the wave-front differing in distance by more than half a wave-length from the latter value, and diminishing therefore the total intensity. According to the strict calculation, the resultant of OA shows a difference of phase slightly less than that given here, and therefore the first maximum will be reached when the O is a little nearer to A, but the difference is negligible.

The amplitude at P at the first maximum will be that due to half the complete wave in addition to that due to the first strip OM_1, or $\cdot5+\cdot6725=1\cdot1725$. This being the amplitude, the intensity will be 1·3748. Fresnel gives for the intensity of the first maximum 1·3707; so that the approximate calculation yields results which for all practical purposes are identical with the true ones. For the subsequent intensities of maxima and minima the agreement is still closer, as will be seen from the following Table :—

	Intensity according to Fresnel.	Intensity from approximate calculation.
First Maximum	1·3707	1·3748
„ Minimum	·7785	·7774
Second Maximum	1·1995	1·1995
„ Minimum	·8433	·8429
Third Maximum	1·1511	1·1509
„ Minimum	·8720	·8718
Fourth Maximum	1·1262	1·1259
„ Minimum	·8892	·8891
Fifth Maximum	1·1103	1·1107
„ Minimum	·9007	·9006
Sixth Maximum	1·0993	1·0994
„ Minimum	·9093	·9092

The irregularity in the differences is partly due to inaccuracy of the last decimal place in the values of $\int \cos v^2\,dv$ and $\sin v^2\,dv$, as given by Fresnel, but it would hardly repay the trouble to recalculate the numbers.

As regards the position of the maxima, they will according to our calculation occur when PA is equal to

$$PO+\frac{3}{8}\lambda,\ PO+\frac{11}{8}\lambda,\ \&c;$$

the minima lying at points for which PA is equal to

$$PO+\frac{7}{8}\lambda,\ PO+\frac{15}{8}\lambda,\ \&c.$$

It is known that these positions agree very well with those obtained by the rigorous analysis; thus Verdet gives as a second approximation for the first maximum

$$PA=PO+\frac{3}{8}\lambda-\cdot0046\lambda,$$

and first minimum

$$PA=PO+\frac{7}{8}\lambda+\cdot0016\lambda,$$

the subsequent maxima and minima agreeing still more closely with the first approximation.

The elementary method which has been described gives therefore results which for an approximate method are of surprising accuracy, if it is considered that no integration has been made use of beyond that implied in the statement that if a large number n of vibrations of equal amplitudes and phases uniformly distributed through two right angles are added up together, the amplitude of the resultant is $2na/\pi$.

The more general proposition, that if a number of vibrations of equal amplitude have phases uniformly distributed through an angle 2θ, the resultant is obtained by reducing in the ratio of $\sin\theta : \theta$ the value calculated on the supposition that they have all the same phase, has many important applications in the theory of diffraction. Several pages are generally devoted to the calculation of the position and intensity of diffraction-fringes produced by a slit on a screen at a great distance. The results obtained may be written down at once from the above proposition, which may be deduced with the help of a series; so that a satisfactory account of the position and intensity of diffraction-bands can be obtained without the help of the integral calculus.

The series

$$S \equiv m_1 - m_2 + m_3 - m_4 + \ldots + m_n, \quad . \quad . \quad . \quad . \quad (1)$$

where the terms alter their value only slowly, occurs frequently in problems on diffraction, and its sum is said to be equal to half the first added to half the last term; but I have not met with a satisfactory proof of this statement. When a proof is attempted the second term is balanced against half the first, and half the third, and so on, but no reason is given why the balance should not be made in another way, and the second term, for instance, balanced against three quarters of the first and one quarter of the third term. The following considerations will show in what cases the addition of the above series may be effected in the manner indicated. We may write the series

$$S \equiv \frac{m_1}{2} + \left(\frac{m_1}{2} - m_2 + \frac{m_3}{2}\right) + \left(\frac{m_3}{2} - m_4 + \frac{m_5}{2}\right) + \ldots + \left(\frac{m_{n-2}}{2} + m_{n-1} + \frac{m_n}{2}\right) + \frac{m_n}{2} \quad . \quad . \quad (2)$$

or

$$S \equiv m_1 - \frac{m_2}{2} - \left[\left(\frac{m_2}{2} - m_3 + \frac{m_4}{2}\right) + \left(\frac{m_4}{2} - m_5 + \frac{m_6}{2}\right) + \ldots + \left(\frac{m_{n-3}}{2} - m_{n-2} + \frac{m_{n-1}}{2}\right)\right] - \frac{m_{n-1}}{2} + m \quad . \quad . \quad . \quad (3)$$

Suppose, in the first place, that each term of the original series has an absolute value which is greater than the arithmetical mean between the preceding and following terms.

From the forms (2) and (3) we see at once that then

$$m_1 - \frac{m_2}{2} + m_n - \frac{m_{n-1}}{2} < S < \frac{m_1}{2} + \frac{m_n}{2}.$$

If m_1 is very nearly equal to m_2, and m_n nearly equal to m_{n-1}, the two limits lie close together, and we may approximately write

$$S = \frac{m_1}{2} + \frac{m_n}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The last term has been taken as positive for the sake of simplicity. It occurs in (4) of course with its proper sign.

If the series is such that the numerical value of each term is *less* than the arithmetical mean of the two terms between which it lies, the same conclusion follows in the same way.

If in the first p terms of the series each term has a greater value, and in the remaining part a smaller value than the arithmetical mean of the preceding and following term, we may break up the series into two, and obtain the sum

$$S = \frac{m_1}{2} \pm \frac{m_p}{2} \mp \frac{m_{p+1}}{2} + \frac{m_n}{2}.$$

It is thus clear that the expressions (4) will be the correct summation only, if the series can be broken up into a small number of separate series for each of which the value of a term is either smaller or greater than the arithmetical mean of the terms between which it stands, so that the sum of all such values as $m_p - m_{p+1}$ may be neglected. In other words, if the absolute values of the terms are plotted as ordinates to equidistant abscissæ, the curve must be either wholly convex or wholly concave, or the number of times the curve changes from concavity to convexity must be negligible compared to the whole number of terms in the series.

A few remarks are suggested by historical considerations. I do not know who first made use of the term "Huyghens zones," but the expression does not seem to me to be altogether appropriate. Huyghens no doubt first divided a wave-front into parts, and considered the effect of the whole wave to be the same as that of the sum of its parts; but the importance of the so-called "Huyghens zone" lies not in the possibility of division but in the particular manner of dividing into elements, by means of radii vectors differing by half a wave-length. This, as far as I know, is exclusively due to Fresnel, who by its means was enabled to draw important

conclusions in a very simple manner. I think, therefore, that the expression Fresnel zones or Fresnel strips would be more appropriate.

Fresnel himself did not fall into the pitfall which is pointed out in this paper. All his statements are well guarded and correct. Lamé, in his Text-Book on Physics (1840), considerably extended Fresnel's reasoning, and drew further conclusions from the division of a plane wave into strips, but he also avoided the algebraic addition of the effects of different strips which have not the same phase.

Verdet was less careful, and through the following passage (*Leçons d'Optique physique*, vol. i. p. 181) is responsible for the idea that the successive strips divided in Fresnel's manner give rise to vibrations of opposite phases irrespective of their distance from the central point :—

" Il est facile de voir que deux arcs élémentaires consécutifs envoient au point P des vitesses de signes contraires ; car à chaque point pris sur l'un de ces arcs correspond un point situé sur l'arc précédent et dont la distance au point P est inférieure d'une demi longueur d'ondulation à celle du premier point au même point P, d'où il resulte que ces deux points envoient à P des vitesses de signes contraires."

The reasoning here is obviously wrong. Consider two successive elements sending vibrations to P which range in phase from 0 to π and from π to 2π respectively. It does not follow that the resultant of one element should have a phase opposite to that of the other element, quite irrespective of the law of distribution of the individual vibrations sent out from different parts of each element. If the vibrations are evenly distributed, Verdet's conclusions would be justified, but the radius vector having a minimum length at the central spot, alters very little near that point. The vibrations from the first element combine at the point P therefore to a resultant having a difference of phase considerably smaller than that calculated from the supposition of an uniform distribution.

I cannot help thinking that writers on Physical Optics have followed too blindly the footsteps of Verdet, whose arguments do not seem to me to be always so conclusive as they are commonly supposed to be.

I have avoided in this paper speaking of a " linear wave," as I believe more harm is done by the introduction of such an idea than can be counterbalanced by the slight simplification of expression. Students who are taught to live only in a two-dimensional space will not be able to make much use of their science in after life.

X. *On Pin-hole Photography.*

By Lord Rayleigh, *Sec. R.S.**

[Plate IV.]

IT has long been known that the resolving power of lenses, however perfect, is limited, and more particularly that the capability of separating close distant objects, *e. g.* double stars, is proportional to aperture. The ground of the limitation lies in the finite magnitude of the wave-length of light (λ), and the consequent diffusion of illumination round the geometrical image of even an infinitely small radiant point. It is easy to understand the *rationale* of this process without entering upon any calculations. At the focal point itself all the vibrations proceeding from various parts of the aperture arrive in the same phase. The illumination is therefore here a maximum. But why is it less at neighbouring points in the focal plane which are all equally exposed to the vibrations from the aperture? The answer can only be that at such points the vibrations are discrepant. This discrepance can only enter by degrees; so that there must be a small region round the focus at any point of which the phases are practically in agreement, and the illumination sensibly equal to the maximum.

These considerations serve also to fix at least the order of magnitude of the patch of light. The discrepancy of phase is the result of the different distances of the various parts of the aperture from the eccentric point in question; and the greatest discrepancy is that between the waves which come from the nearest and furthest parts of the aperture. A simple calculation shows that the greatest difference of distance is expressed by $2rx/f$, where $2r$ is the diameter of the aperture, f the focal length, and x the linear eccentricity of the point under consideration. The question under discussion is at what stage does this difference of path introduce an important discrepancy of phase? It is easy to recognize that the illumination will not be greatly reduced until the extreme discrepancy of phase reaches half a wave-length. In this case

$$2x = f\lambda/2r,$$

which may be considered to give roughly the diameter of the patch of light. If there are two radiant points, the two representative patches will seriously overlap, unless the distance of their centres exceed $2x$. Supposing it to be equal to $2x$, which corresponds to an angular interval $2x/f$, we see that

* Communicated by the Author.

the double radiant cannot be resolved in the image, unless the angular interval exceed $\lambda/2r$.

Experiment* shows that the value thus roughly estimated is very near the truth for a rectangular aperture of width $2r$. If the aperture be of circular form, the resolving power is somewhat less, in the ratio of about 1·1 : 1.

It is therefore not going too far to say that there is nothing better established in optics than the limit to resolving power as proportional to aperture. On the other hand, the focal length is a matter of indifference, if the object-glass be perfect.

This is one side of the question before us. We now pass on to another, in which the focal length becomes of paramount importance.

"The function of a lens in forming an image is to compensate by its variable thickness the differences in phase which would otherwise exist between secondary waves arriving at the focal point from various parts of the aperture. If we suppose the diameter of the lens ($2r$) to be given, and its focal length (f) gradually to increase, these differences of phase at the image of an infinitely distant luminous point diminish without limit. When f attains a certain value, say f_1, the extreme error of phase to be compensated falls to $\frac{1}{4}\lambda$. Now, as I have shown on a previous occasion†, an extreme error of phase amounting to $\frac{1}{4}\lambda$, or less, produces no appreciable deterioration in the definition; so that from this point onwards the lens is useless, as only improving an image already sensibly as perfect as the aperture admits of. Throughout the operation of increasing the focal length, the resolving power of the instrument, which depends only upon the aperture, remains unchanged; and we thus arrive at the rather startling conclusion that a telescope of any degree of resolving power might be constructed without an object-glass, if only there were no limit to the admissible focal length. This last proviso, however, as we shall see, takes away almost all practical importance from the proposition.

"To get an idea of the magnitudes of the quantities involved, let us take the case of an aperture of $\frac{1}{5}$ inch, about that of the pupil of the eye. The distance f_1, which the actual focal length must exceed, is given by

$$\sqrt{\{f_1^2 + r^2\}} - f_1 = \tfrac{1}{4}\lambda;$$

so that [approximately]

$$f_1 = 2r^2/\lambda.$$

* "On the Resolving Power of Telescopes," Phil. Mag. August 1880.

† Phil. Mag. November 1879.

Thus, if $\lambda = 1/40{,}000$, $r = 1/10$,

$$f_1 = 800.$$

The image of the sun thrown on a screen at a distance exceeding 66 feet, through a hole $\frac{1}{5}$ inch in diameter, is therefore at least as well defined as that seen direct. In practice it would be better defined, as the direct image is far from perfect. If the image on the screen be regarded from a distance f_1, it will appear of its natural angular magnitude. Seen from a distance less than f_1, it will appear magnified. Inasmuch as the arrangement affords a view of the sun with full definition [corresponding to aperture] and with an increased apparent magnitude, the name of a telescope can hardly be denied to it.

"As the minimum focal length increases with the square of the aperture, a quite impracticable distance would be required to rival the resolving power of a modern telescope. Even for an aperture of four inches f_1 would be five miles"*.

A more practical application of these principles is to be found in landscape photography, where a high degree of definition is often unnecessary, and where a feeble illumination can be compensated by length of exposure. In a recent communication to the British Association† it was pointed out that a suitable aperture is given by the relation

$$2r^2 = f\lambda ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and a photograph was exhibited in illustration of the advantage to be derived from an increase of f. The subject was a weather-cock, seen against the sky, and it was taken with an aperture of $\frac{1}{16}$ inch, and at a distance of 9 feet. The amount of detail in the photograph is not markedly short of that observable by direct vision from the actual point of view. The question of brightness was also considered. As the focal length increases, the brightness (B) in the image of a properly proportioned pin-hole camera diminishes. For

$$B \propto r^2/f^2 \propto r^2\lambda^2/r^4 \propto \lambda^2/r^2 \propto \lambda/f. \quad . \quad . \quad . \quad (2)$$

There will now be no difficulty in understanding why a certain aperture is more favourable than either a larger or a smaller one, when f and λ are given. If the aperture be very small, the definition is poor even if the aid of a lens be

* "On Images formed without Reflection or Refraction," Phil. Mag. March 1881.

† Brit. Assoc. Report, 1889, p. 493.

invoked. If, on the other hand, the aperture be large, the lens becomes indispensable. The size of the aperture should accordingly be increased up to the point at which the lens is sensibly missed; and this, as we have seen, will occur in the neighbourhood of the value determined by (1). A more precise calculation can be made only upon the basis of a detailed knowledge of the distribution of light in the image.

The question of the best size of aperture for a pin-hole camera was first considered by Petzval*. His theory, though it can hardly be regarded as sound, brings out the failure of definition when the aperture is either too large or too small, and, as is very remarkable, gives (1) as the best relation between r, f, and λ. The argument is as follows:—If the hole be very small, the diameter of the patch of light representative of a luminous point is given by

$$D = f\lambda/r,$$

the measurement being made up to the first blackness in the diffraction-pattern. "This formula is only an approximate one, applicable when r is very small; in the case of a larger aperture, its diameter must be added to the value above given, that is to say,

$$D = 2r + f\lambda/r.$$

From the last formula we can at once deduce the best value for r; in other words, the size of the aperture which corresponds to the least possible value of D, and therefore to the sharpest possible image. In fact, differentiating the last expression, and setting in the ordinary manner, $dD/dr = 0$, we find at once

$$r = \surd(\tfrac{1}{2} f\lambda),$$

which corresponds to

$$D = 2\surd(2f\lambda).$$"

The assumption that intermediate cases can be represented by mere addition of the terms appropriate in the extreme cases of very large and very small apertures appears to be inadmissible.

The complete determination of the image of a radiant point as given by a small aperture is a problem in diffraction, solved only within the last years by Lommel†. In view of the

* *Wien. Sitz. Ber.* xxvi. p. 33 (1857); Phil. Mag. xvii. (1859) p. 1.

† "Die Beugungserscheinungen einer kreisrunden Öffnung und eines kreisrunden Schirmchens," *Aus den Abhandlungen der k. bayer. Akademie der Wiss.* ii. Cl. xv. Bd. ii. Abth. (Munchen, 1884.)

practical application to pin-hole photography, I have thought that it would be interesting to adapt Lommel's results to the problem in hand, and to exhibit upon the same diagram curves showing the distribution of illumination in various cases. For the details of the investigation reference must be made to Lommel's memoir, or to the account of it in the *Encyclopædia Britannica*, art. "Wave Theory," p. 444. But it may be well to state the results somewhat fully.

In the following formulæ a is the distance from the radiant point to the aperture, b from the aperture to the screen upon which the image is formed. The circumstances being symmetrical about a line through the radiant point and the centre of the circular aperture (radius r), the illumination I^2 will be the same at all points of the screen equally distant ζ from the axis, and the problem to be solved is the determination of I^2 as a function of ζ for given values of a, b, r, and λ. Lommel finds that

$$I^2=\frac{1}{a^2b^2\lambda^2}(C^2+S^2), \quad . \quad . \quad . \quad . \quad (3)$$

where

$$C=\iint \cos\left(\tfrac{1}{2}\kappa\rho^2-l\rho\cos\phi\right).\rho\,d\rho\,d\phi, \quad . \quad . \quad . \quad (4)$$

$$S=\iint \sin\left(\tfrac{1}{2}\kappa\rho^2-l\rho\cos\phi\right).\rho\,d\rho\,d\phi, \quad . \quad . \quad . \quad (5)$$

and the following abbreviations are introduced :—

$$\frac{2\pi}{\lambda}\frac{a+b}{2ab}=\tfrac{1}{2}\kappa, \quad \frac{2\pi\zeta}{b}=l. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The above corresponds to an incident wave whose intensity at the aperture is measured by $1/a^2$. The integration is to be taken over the area of the aperture, that is from $\phi=0$ to $\phi=2\pi$, and from $\rho=0$ to $\rho=r$. If we introduce the notation of Bessel's functions, we have

$$C=2\pi\int_0^r J_0(l\rho)\cos\left(\tfrac{1}{2}\kappa\rho^2\right).\rho\,d\rho, \quad . \quad . \quad . \quad . \quad (7)$$

$$S=2\pi\int_0^r J_0(l\rho)\sin\left(\tfrac{1}{2}\kappa\rho^2\right).\rho\,d\rho. \quad . \quad . \quad . \quad . \quad (8)$$

By integration by parts of these expressions Lommel develops series suitable for calculation. Setting

$$\kappa r^2=y \quad lr=z, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

he finds in the first place

$$C=\pi r^2\left\{\frac{\cos\frac{1}{2}y}{\frac{1}{2}y}U_1+\frac{\sin\frac{1}{2}y}{\frac{1}{2}y}U_2\right\}, \quad . \quad . \quad . \quad (10)$$

$$S=\pi r^2\left\{\frac{\sin\frac{1}{2}y}{\frac{1}{2}y}U_1-\frac{\cos\frac{1}{2}y}{\frac{1}{2}y}U_2\right\}, \quad . \quad . \quad . \quad (11)$$

where

$$U_1=\frac{y}{z}J_1(z)-\frac{y^3}{z^3}J_3(z)+\frac{y^5}{z^5}J_5(z)-\ldots, \quad . \quad . \quad (12)$$

$$U_2=\frac{y^2}{z^2}J_2(z)-\frac{y^4}{z^4}J_4(z)+\ldots. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

These series are convenient when y is less than z.

The second set of expressions are

$$C=\pi r^2\left\{\frac{2}{y}\sin\frac{z^2}{2y}+\frac{\sin\frac{1}{2}y}{\frac{1}{2}y}V_0-\frac{\cos\frac{1}{2}y}{\frac{1}{2}y}V_1\right\}, \quad . \quad . \quad (14)$$

$$S=\pi r^2\left\{\frac{2}{y}\cos\frac{z^2}{2y}-\frac{\cos\frac{1}{2}y}{\frac{1}{2}y}V_0-\frac{\sin\frac{1}{2}y}{\frac{1}{2}y}V_1\right\}, \quad . \quad . \quad (15)$$

where

$$V_0=J_0(z)-\frac{z^2}{y^2}J_2(z)+\frac{z^4}{y^4}J_4(z)-\ldots, \quad . \quad . \quad (16)$$

$$V_1=\frac{z}{y}J_1(z)-\frac{z^3}{y^3}J_3(z)+\ldots. \quad . \quad . \quad . \quad . \quad (17)$$

These series are suitable when z/y is small.

When the primary wave is complete, $r=\infty$, and we have at once from the second set of expressions

$$C_\infty=\frac{2\pi}{\kappa}\sin\frac{l^2}{2\kappa}, \quad S_\infty=\frac{2\pi}{\kappa}\cos\frac{l^2}{2\kappa}, \quad . \quad . \quad . \quad (18)$$

so that

$$I_\infty^2=\frac{C_\infty^2+S_\infty^2}{a^2b^2\lambda^2}=\frac{1}{(a+b)^2}, \quad . \quad . \quad . \quad . \quad (19)$$

as we know it should be.

At the central point of the image where $z=0$, $V_0=1$, $V_1=0$,

$$C=\pi r^2\frac{\sin\frac{1}{2}y}{\frac{1}{2}y}, \quad S=\pi r^2\left\{\frac{2}{y}-\frac{\cos\frac{1}{2}y}{\frac{1}{2}y}\right\},$$

and

$$I^2=\frac{4}{(a+b)^2}\sin^2\left(\frac{\pi r^2}{\lambda}\frac{a+b}{2ab}\right). \quad . \quad . \quad . \quad . \quad (20)$$

In general by (10), (11),

$$C^2+S^2=\frac{4\pi^2r^4}{y^2}\{U_1^2+U_2^2\}=\pi^2r^4\cdot M^2, \quad . \quad . \quad (21)$$

if with Lommel we set

$$M^2=\left(\frac{2}{y}U_1\right)^2+\left(\frac{2}{y}U_2\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Also

$$I^2=\frac{\pi^2r^4}{a^2b^2\lambda^2}\cdot M^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

In these formulæ U_1^2, U_2^2, and therefore by (22), (23) M^2 and I^2 are known functions of y and z. The connexion with r and ζ is given by the relations

$$y=\frac{2\pi r^2}{\lambda}\frac{a+b}{ab}, \quad z=\frac{2\pi r\zeta}{\lambda b}. \quad . \quad . \quad . \quad . \quad (24)$$

In Lommel's memoir are given the values of M^2 for integral values of z from 0 to 12 when y has the values π, 2π, 3π, &c. If we regard a, b, λ as given, each of these Tables affords a knowledge of the distribution of illumination as a function of ζ for a certain radius of aperture by means of the two equations (24). In each case ζ is proportional to z; but in comparing one case with another we have to bear in mind that the ratio of ζ to z varies. As our object is to compare the distributions of illumination when the aperture varies, we must treat ζ, and not z, as the abscissa in our diagrams. Another question arises as to how the scale of the ordinate I^2 should be dealt with in the various cases. If we take (23) as it stands we shall have curves corresponding to the same actual intensity of the radiant point. For some purposes this might be desirable; but in the application to photography the deficiency of illumination when the aperture is much reduced would always be compensated by increased exposure. It will be more practical to vary the scale of ordinates from that prescribed in (23), so as to render the illumination corresponding to an extended source of light, such as the sky, the same in all cases. We shall effect this by removing from the right-hand member of (23) a factor proportional to the area of aperture, proportional that is to r^2, or y. Thus for any value of y equal to $s\pi$, we shall require to plot as ordinate, not M^2 simply, but sM^2, and as abscissa, not z simply, but $z/\sqrt{s}$. The following are at once deduced from Lommel's tables III.–VI.

$y=\pi$.

z.	$z/\sqrt{1}=z$.	M^2.
0	0	·8106 Max.
1	1	·6286
2	2	·2772
3	3	·0623
4	4	·0269
5	5	·0306
6	6	·0121
7	7	·0018
8	8	·0051
9	9	·0037
10	10	·0004
11	11	·0013
12	12	·0016
3·8317	.....	·0263 Min.
4·7153	.....	·0320 Max.
7·0156	.....	·0018 Min.
8·3060	.....	·0055 Max.
10·1735	.....	·0003 Min.
11·5785	.....	·0019 Max.

$y=2\pi$.

z.	$z/\sqrt{2}$.	$2M^2$.
0	·000	·8106 Max.
1	·707	·6316
2	1·414	·3117
3	2·121	·1560
4	2·829	·1438
5	3·536	·1077
6	4·243	·0426
7	4·950	·0200
8	5·657	·0227
9	6·364	·0125
10	7·071	·0034
11	7·778	·0053
12	8·485	·0046
3·5977	2·544	·1440 Min.
3·8317	2·710	·1442 Max.
7·0156	4·961	·0198 Min.
7·8879	5·578	·0229 Max.
10·1735	7·193	·0032 Min.
11·4135	8·070	·0059 Max.

$y = 3\pi$.

z.	$z/\sqrt{3}$.	$3M^2$.
0	·000	·2702 Max.
1	·577	·2159
2	1·154	·1631
3	1·732	·2110
4	2·310	·2449
5	2·887	·1734
6	3·464	·0916
7	4·041	·0739
8	4·619	·0651
9	5·195	·0335
10	5·773	·0156
11	6·350	·0178
12	6·927	·0122
1·9969	1·153	·1631 Min.
3·8317	2·212	·2467 Max.
7·0156	4·050	·0737 Min.
7·0878	4·092	·0739 Max.
10·1735	5·871	·0154 Min.
11·0361	6·374	·0178 Max.

$y = 4\pi$.

z.	$z/2$.	$4M^2$.
0	·000	·0000 Min.
1	·500	·0056
2	1·000	·0609
3	1·500	·1594
4	2·000	·1947
5	2·500	·1515
6	3·000	·1293
7	3·500	·1399
8	4·000	·1148
9	4·500	·0658
10	5·000	·0484
11	5·500	·0458
12	6·000	·0280
3·8317	1·9158	·1961 Max.
5·8978	2·9489	·1291 Min.
7·0156	3·5078	·1399 Max.
10·1735	5·0867	·0483 Min.
10·3861	5·1930	·0483 Max.

As it appeared desirable to trace the curve corresponding to a smaller value of y than any given by Lommel, I have calcu-

lated by means of (12), (13) the value of $\frac{1}{2}M^2$, that is of

$$\frac{8}{\pi^2}(U^2{}_1+U_2{}^2),$$

corresponding to $z=0$, 1, 2, 3, 4.

The results are as follows :—

$y=\frac{1}{2}\pi$.

z.	$\sqrt{2}.z$.	$\frac{1}{2}M^2$.
0	·000	·4748
1	1·414	·3679
2	2·828	·1590
3	4·243	·0272
4	5·657	·0041

The various curves, or rather the halves of them, are plotted in Plate IV., and exhibit to the eye the distribution of light in the images corresponding to the different apertures. It is at once evident that $y=\frac{1}{2}\pi$ is too small, and that $y=3\pi$ is too great. The only question that can arise is between $y=\pi$ and $y=2\pi$. The latter has decidedly the higher resolving power, but the advantage is to some extent paid for in the greater diffusion of light outside the image proper. In estimating this we must remember that the amount of light is represented, not by the *areas* of the various parts of the diagrams, but by the *volumes* of the solids formed by the revolution of the curves round the axis of I^2. In virtue of the method of construction the total volume is the same in all cases. The best aperture will thus depend in some degree upon the subject to be represented; but there is every reason to think that in general $y=2\pi$ will prove more advantageous than $y=\pi$. It will be convenient to recall that

$$y/\pi=\frac{2r^2}{\lambda}\frac{a+b}{ab};$$

or, if we write $a=\infty$, $b=f$,

$$y/\pi=2r^2/\lambda f. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The curve $y=\pi$ thus corresponds to (1); and we conclude that the aperture may properly be somewhat enlarged so as to make

$$r^2=\lambda f. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

In the general case when a is finite, y/π represents four times

the number of wave-lengths by which the extreme ray is retarded relatively to the central ray ; for

$$\frac{\sqrt{(a^2+r^2)}+\sqrt{(b^2+r^2)}-a-b}{\lambda} = \frac{r^2}{2\lambda}\frac{a+b}{ab}, \text{ approximately.}$$

According to (26) the aperture should be enlarged until the retardation amounts to $\frac{1}{2}\lambda$.

In the image of a double star the curves of brightness proper to the two components are superposed. If the components are equal, resolution will be just beginning when the distance of the geometrical images asunder is the double of the value of ζ for which I^2 has about one-half its maximum value. By inspection of the curve for $y=2\pi$ we see that there will not be much appearance of resolution until $z/\sqrt{2}=1{\cdot}5$. The corresponding angular interval between the two components is

$$\frac{2\zeta}{f} = \frac{1{\cdot}5\times\sqrt{2}}{\pi}\sqrt{\left(\frac{\lambda}{f}\right)}. \quad . \quad . \quad . \quad . \quad (27)$$

This may be regarded as defining the maximum separating power as a function of λ and f.

Passing on from the theoretical discussion, I will now describe certain laboratory observations upon the defining power of various apertures. A succession of such, of gradually increasing magnitude, were perforated in a piece of thin sheet zinc, and were measured under the microscope. The diameters, in fractions of an inch, are as follows :—

(1)	(2)	(3)	(4)	(5)	(6)
·0210,	·0240,	·0262,	·0290,	·0326,	·0366.

The objects, whose images were examined, are (1) a grating cut out of sheet zinc, and (2) a pair of equal round holes a quarter of an inch apart. The period of the grating is also a quarter inch, and the transparent and opaque parts are equally wide. Behind the grating, or double hole, was placed a paraffin lamp and a large condensing lens. The distance a between the objects and the apertures under test was about 18 feet.

The best image with a given aperture is obtained by bringing the eye immediately behind, without the use of a focusing lens. But the image formed at a sufficient distance beyond, and examined with a focusing glass of low power, is nearly as good. Thus at a sufficient distance (b) the

largest aperture gives the best image, but at a *given* distance behind the case is otherwise. For example, when the image was formed at 8 inches distance, (2) and (3) were about equal as respects the double hole, while (1) was decidedly inferior, and that not apparently from want of light. In the case of the grating (3) had perhaps the advantage over (2).

A photograph of the double hole was now taken under the same circumstances with an exposure of 80 minutes. Aperture (2) was here decidedly better than (3), and (1) was almost as good as (2). The (negative) image formed by (5) exhibited a pair of white spots near the centre of a patch of black, corresponding to the state of things indicated in the curve $y=4\pi$. The difference between the photograph and the result obtained by eye observation is readily explained by the smaller effective wave-length in the former case.

The difference just spoken of is intensified when the light is white. In one experiment upon cloud-light $a=21$ feet, $b=10$ inches. In the resulting photograph, obtained upon an Ilford plate with an exposure of 30 minutes, the image from (2) was decidedly the best.

We may utilize the last result to calculate the relation between aperture and focus most suitable for out of door photography. We have

$$(2r)^2\left(\frac{1}{a}+\frac{1}{b}\right)=(\cdot0240)^2\left(\frac{1}{252}+\frac{1}{10}\right)$$

$$=10^{-5}\times5\cdot99 \text{ inches}=10^{-4}\times1\cdot52 \text{ centim.}$$

Thus, if $a=\infty$, as may usually be supposed in landscape-photography, the most favourable diameter of aperture is given by

$$(2r)^2/f=10^{-5}\times6\cdot0 \text{ inches}=10^{-4}\times1\cdot5 \text{ centim.},$$

the first number being employed if r and f are measured in inches, and the latter when the measures are in centimetres*. If $f=12$ inches, $2r=\cdot027$ inch. If $f=7\times12=84$ inches, $2r=\cdot071$ inch.

The experimental determination of the best value of y is more easily effected by eye observations. In order to render the wave-length more definite an orange-red glass was employed. With $a=18$ feet, $b=8$ inches, the image formed by aperture (3) was judged to be decidedly the best, (2) was

* The effect of varying the diameter of aperture in photographic landscape work has been tested by Capt. Abney; but I am not in possession of the data as to focal length necessary for a comparison with the above.

next, while (1) and (4) were decidedly behind. Thus we may take as the most favourable aperture $2r = \cdot026$ inch.

The mean wave-length of the light employed was found with the aid of a grating by a comparison with a soda flame :—

$$\text{Mean } \lambda : \lambda_D = 239 : 226 ;$$

so that

$$\lambda = \frac{239}{226} \times 5\cdot89 \times 10^{-5} = 6\cdot23 \times 10^{-5} \text{ centim.}$$

Hence

$$y/\pi = \frac{2r^2}{\lambda}\left(\frac{1}{a} + \frac{1}{b}\right) = \frac{(\cdot026)^2}{2}\,\frac{7}{54}\,\frac{2\cdot54 \times 10^5}{6\cdot23} = 1\cdot79,$$

agreeing very well with what was expected from the curves.

If we now assume that the best value of y is 1·8, we can calculate backwards from the photographic results to find the mean λ there effective. We have

$$10^{-4} \times 1\cdot52 = (2r)^2\left(\frac{1}{a} + \frac{1}{b}\right) = \frac{2\lambda y}{\pi} = 2\lambda \times 1\cdot8;$$

whence

$$\lambda = 4\cdot2 \times 10^{-5} \text{ centim.},$$

a little less than that belonging to Fraunhofer's line G.

To test the improvement of definition which according to (27) accompanies an increase of f, I have used an aperture of ·07 inch and a focal length of 7 feet. The aperture was perforated in sheet zinc, and was placed in the shutter of a room otherwise completely darkened. The subject was a group of cedars, and, being somewhat dark in the shadows, required an exposure of about an hour and a half, even in sunshine. The resulting 12 × 10-inch photographs fully bear out expectations. To appear in natural magnitude the pictures would of course need to be held at 7 feet distance from the eye ; but even at 3 or 4 feet the apparent definition is sufficient. I have also taken panoramic pictures with an aperture of ·027 inch and a focal distance of 12 inches ; but in this case there is nothing that could not equally well be done with an ordinary portable camera.

Terling Place, Witham, Essex,
Dec. 2, 1890.

XI. *The Problem of the Behaviour of the Magnetic Field about a Revolving Magnet.* *By* S. Tolver Preston*.

WHEN the earth revolves on its axis, does the magnetic field (the earth being regarded as a magnet) revolve with it?

With the view to test this question of the behaviour of the magnetic field about a revolving magnet, I have proposed (communicated in an unpublished letter) the following experiment whereby some phenomena are in question which (without probably involving any novelty in point of theory) might seem to merit a passing notice. I will briefly indicate this here.

Let m (fig. 1) represent a cylindrical bar-magnet: the

Fig. 1.
Hypothesis (1).

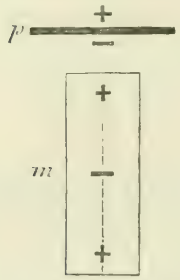
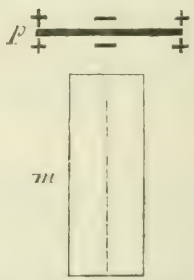


Fig. 2.
Hypothesis (2).



cylindrical form may be taken for simplicity here. Let the magnet be rotated about its vertical axis below the circular flat plate or disk (of metal) p, seen edgeways in the diagram.

Then under hypothesis (1), that the magnetic field remains stationary or fixed while the magnet revolves (as Faraday thought† he had proved), the magnet will revolve through *its own field*, and therefore become charged up at its poles and equatorial part by electricity of opposite sign, dependent on the direction of rotation, as fig. 1 indicates. This magnetic field (as it does not rotate) cannot electrodynamically influence the disk p; but—and here is the point I wish to call attention to—this charge at the upper pole of the magnet can act by *static* electric induction across the layer of air, and so produce an opposite charge below the disk p. The disk is therefore

* Communicated by the Author.

† Two papers by me in the Philosophical Magazine for February and March 1885 may be referred to in connexion with this. The present paper, however, is a separate one in itself, or is original and unpublished.

charged negatively below and positively above in the present case (fig. 1). It remains, then, to investigate the nature of this charge in order to prove which hypothesis is true—*i. e.* in order to show whether the magnetic field rotates with the magnet or does not do so.

For it will be perceived that under hypothesis (2), when the magnetic field (*per contra*) is assumed to revolve with the magnet, the field will cut through or intersect the disk *p* (fig. 2) as the magnet revolves; and so the disk will, according to known principles, be charged through electrodynamic* induction with electricity of opposite sign at its centre and periphery respectively, as fig. 2 shows.

But it will be observed that the decomposition of the electricity in the disk takes place under hypothesis (2) in a direction *at right angles* to that which occurs under hypothesis (1). So that it will be evident that we have a physical test between the two opposite hypotheses here. Under hypothesis (1), namely, the disk is polarized by electro*static* induction in the direction of its thickness; and under hypothesis (2) the disk is polarized by electro*dynamic* induction in a direction at right angles to the former, viz. transversely, or along all its radii, as fig. 2 indicates. These diverse physical effects then, as it appears, are capable of constituting a test to decide between the two rival hypotheses.

But I am informed by Prof. H. Hertz, of Bonn, to whom I had communicated the above by letter, that with a normally sensitive electrometer a considerable velocity of rotation with a magnet of large size would be calculably required in order to produce a distinct deflexion under either hypothesis: and facts of this kind discourage from trying the experiment.

I would therefore venture to ask—in order to facilitate the experiment—whether with the aid of Mr. Vernon Boys's discoveries, or those of others, it is not possible to bring the electrometer to a much higher degree of sensitiveness? Prof. Hertz lays stress on the great interest attaching to the inquiry, and agrees that the conditions of test as above proposed should† be capable of deciding this question,—presup-

* This charge will react electrostatically on the magnet, to produce a feeble (secondary) charge there, which need not be taken into account, as it does not affect our experiment.

† It may be, of course, that the magnetic field *partly* partakes of the motion of the revolving magnet, or that something between the two hypotheses is true. Then a modified distribution of charge on the disk would obviously present itself, consistent with such conditions. In other words, if neither vertical nor horizontal polarization of the disk were found to be precise (but a superposition of the one upon the other), then this would obviously indicate that the field partly shared the rotation of the magnet, so that both magnet and disk were intersected by the field.

posing of course sufficient instrumental means. It seems therefore that a specially sensitive electrometer would be doubly effective here, as eliminating the shock and concussion inevitably attendant on a high velocity and a large magnet, which tend to conceal delicate observations.

Hamburg, December 13, 1890.

XII. *Alternate Current-Condensers.* *By* J. Swinburne*.

THOUGH condensers have been proposed for various methods of distribution of electrical power, schemes involving the use of them have never developed enough for alternating current-condensers to be made commercially. It is generally assumed that there is no difficulty in making them ; all that is needed is to separate a number of thin plates by means of sheets of insulating material.

The first difficulty is insulation. If a condenser is to take 2000 effective volts, the insulation must be very good. Too great thickness of dielectric cannot be allowed, as that would lessen the capacity, and increase the cost of material. The surface of such a condenser for, say, ten amperes is about a thousand square feet, and the problem of making a thousand square feet of thin insulating material that will safely stand 2000 volts is not easy. I have made samples which, though only a little over a tenth of a millimetre thick, would stand 8000 effective volts for some time before breaking down. When made up into a large condenser, two or three thousand volts would generally break it down in a few hours.

Insulation is not by any means the only difficulty, however ; there is another, which is probably intimately connected with it, and that is absorption of electric power in the dielectric, and consequent heating. It is well known that Leyden jars get hot if charged and discharged frequently ; and also that the phenomenon of electric absorption is manifested. When there is absorption, the current out of the condenser is not proportional to the rate of decrease of the electromotive force, and probably the current into it is not proportional to the rate of increase. This means that the condenser absorbs energy and converts it into heat.

Such questions have been frequently studied in connexion with curves of sines, but it is easier to show the truth of this generally. Let C be the current, E the electromotive force,

* Communicated by the Physical Society : read December 12, 1890.

K the capacity, and t the time. Then

$$C = K\frac{dE}{dt},$$

and the power spent at any instant,

$$EC = EK\frac{dE}{dt}.$$

If e is the maximum electromotive force, the work done in charging the condenser is thus

$$K\int_0^e E\,dE = \tfrac{1}{2}Ke^2,$$

the ordinary expression. On discharging, the work absorbed is

$$K\int_e^0 E\,dE \quad \text{or} \quad -\tfrac{1}{2}Ke^2.$$

It is equally easy to show that no power is absorbed in the case of an induction-coil with no hysteresis, without assuming the pressure to vary harmonically.

If C does not vary as the rate of increase or decrease of E, but is greater on charging and less on discharging, power is absorbed. A hysteresis curve, like those we are accustomed to in iron, can be plotted in the case of a condenser. It has no very close analogy with the case of iron, however.

At first it might seem that absorption might be neglected as too trifling to matter in commercial work. This, however, is not the case. Some condensers about a foot square and an inch thick absorbed over half a horse-power, and soon rose above the temperature of boiling water.

According to Maxwell's theory, the absorption of power is just as easily explained as the time-lag in discharge. Suppose the dielectric is paper soaked in melted paraffin, and suppose the fibres of paper do not insulate and that the paraffin does. When the plates are charged, a fibre running part of the way across the dielectric finds its ends at different potentials ; so a current is set up to equalize them. This current means loss of power by heat. It also increases the capacity of the condenser. An increase of the capacity of the condenser when the pressure is increasing, or after it is applied, means increased energy put into the condenser. If the capacity of the condenser were constant, the current into it would be proportional to the rate of increase of the electromotive force, and no power would be absorbed in a period ; but if the capacity is increased as the pressure rises and decreased as it

falls, there is an extra current produced which is not proportional to the rate of increase of the electromotive force, and this supplies the loss in the condenser. The condenser may still show perfect insulation under a direct pressure. According to this theory, absorption is necessarily accompanied by an increase of capacity. This is important in connexion with the electromagnetic theory of light. Absorption would always increase the apparent capacity of a condenser, so that determinations of specific inductive capacity of absorptive dielectrics would come out too high. The dielectrics which come out too high, such as glass, are just those which heat most. The energy absorbed in a given dielectric would be a function of the frequency and the resistance of the conducting parts. It is thus possible that a dielectric might be opaque to light, and diathermanous if the resistance is comparatively low, or transparent to light, but not to dark heat if it is somewhat higher. Similarly a Leyden jar, which absorbs power when connected to an alternating dynamo, may lose little of its energy internally when discharged oscillatorily by a spark. The case of a fibrous imperfect insulator embedded in a perfect insulator is not susceptible of mathematical treatment and was not taken by Maxwell. Mica is perhaps a better example. It is a good insulator, but gets very hot. If a thin plate is put between two sheets of tinfoil, heating soon shows. Here we have tinfoil, then a stratum of air, then mica, which is itself stratified, then air, then tinfoil again. The static attraction presses the foil close against the mica, still there is air. Unless the mica is very thick, the fall of potential between the plates is so rapid that the air breaks down and there is a disruptive discharge between the foil and the mica. This actually occurs; there appears to be a luminous layer of minute blue sparks under the foils, and there is a strong smell of ozone. The discharge under the foils, which is rendered visible by the transparency of the mica, must not be confused with the brush-discharge round the edges of the foil, which differs in appearance. There is considerable heating even when the foil is affixed with paraffin-wax so that there is no air.

Of course mica, being stratified, may consist of alternate sheets of some imperfect conductor and an insulator. It is more difficult to find a reason why glass should heat. At high temperatures it is an electrolyte, and it has no definite solidifying-point, so it may be partially electrolytic at ordinary temperatures. Such an explanation can hardly be applied to such a substance as celluloid. This is a very perfect insulator, at least till it breaks down disruptively, and it

seems to be homogeneous, and is not hygroscopic, yet it heats considerably.

For commercial condensers the choice of insulating material is limited. Most work has been done on condensers with paper and hydrocarbon insulation. It is difficult to know whether a fault lies in the paper or in the hydrocarbon. The paper is baked at a high temperature, and all temperatures and times of baking have been tried. Paper goes on giving off water till there is nothing but a charred brittle mass left. Many hydrocarbons contain enough water to prevent, for instance, their dissolving rubber. Phosphoric anhydride was used to dry several samples, but seemed to do little good, in fact the crude hydrocarbon was often better. Papers vary astonishingly in their behaviour. Mr. Bourne, who has been working at these things for some months, has tried almost every conceivable way of making condensers. We are just beginning to succeed, but it is more by chance than anything else. We see no reason why one particular kind of paper and one particular kind of hydrocarbon should be better than the others.

Want of homogeneity in the dielectric of a condenser, or of any cable, may lead to disruptive discharges, or breakdowns. For instance, if a dielectric is made up of portions with inductive capacities of 3 and 1 respectively, the parts with a high inductive capacity may arrange themselves so that the "electric displacement" in the other is so great that a disruptive discharge ensues. For instance, if two conducting plates are 3 millim. apart in air, with enough pressure to spark over 2 millim., and if a 2-millim. slab of a dielectric with a specific inductive capacity of 3 is put in, the fall of potential over the air is nearly doubled, and it breaks down and starts a short circuit.

Loss of power in dielectrics is not confined to condensers; it may be very serious in cables. A condenser that heated excessively was made like the Deptford mains. The dielectric was very much thinner in proportion to the pressure, and allowing the loss per cubic centimetre to vary as the square of the pressure on its sides, a Deptford main would have a loss of, very roughly, 7000 watts in the dielectric. It does not follow that this is the exact loss in a Deptford main. Very small differences in the constitution of the dielectric cause large variations in the power wasted. The loss may therefore be very much greater or very much less. Taking the specific inductive capacity of the dielectric as 2, a seven-mile main has a capacity of 2 microfarads. With 10,000 volts at a frequency of 80, this takes 10 amperes and 100,000

"apparent" watts ; 7000 watts is only a small percentage of this.

Another unexpected effect has occurred at Deptford. There is an extraordinary rise of pressure. No authoritatively accurate accounts have been published, so it is difficult to say what has happened ; but it is said that when the mains are put on the pressure rises. This is generally explained by saying the mains have capacity, and there is self-induction in the circuit, and the capacity and self-induction have a period which corresponds with the frequency of the dynamo, so that the system sympathises, or acts as a sort of electric resonator, thus giving abnormally high pressure. A little consideration will show that this theory is untenable. With such a capacity as that of the Deptford cables the self-induction would have to be enormous.

Let the capacity of the cable be K, and the self-induction of the circuit L, in farads and henries or quadrants. Call E and C the electromotive force and current respectively. Then

$$E = L\frac{dC}{dt}$$

and

$$C = -K\frac{dE}{dt}.$$

Combining these equations,

$$\frac{d^2E}{dt^2} = -\frac{E}{KL};$$

so

$$\frac{dE}{dt}\frac{d^2E}{dt^2} = -\frac{E}{KL}\frac{dE}{dt};$$

and integrating,

$$\left(\frac{dE}{dt}\right)^2 = -\frac{1}{KL}(E^2 + a).$$

where a is a constant ;

or

$$\frac{dE}{dt} = -\frac{1}{\sqrt{KL}}\sqrt{(E^2 + a)};$$

so

$$\frac{\sqrt{KL}\,dE}{\sqrt{E^2 + a}} = -dt,$$

and integrating,

$$\sqrt{KL}\cos^{-1}\frac{E}{a} = t.$$

therefore

$$E \propto \cos \frac{t}{\sqrt{KL}}$$

and

$$T = 2\pi \sqrt{KL}$$

When a charged condenser is short-circuited through a circuit with self-induction only, oscillation is produced, the current and pressure both varying harmonically with a frequency of $1/2\pi \sqrt{KL}$.

In the Deptford case, with a capacity of two microfarads and a period of 0·0125, the self-induction needed would be half a henry. A choking coil with such a coefficient of self-induction wound to carry 250 amperes, which, I understand, is the load of one main, would take 64,000 volts to get the current through. A transformer only acts on the circuit as a choking coil to the small extent due to the waste induction in it. If built on the lines of commercial transformers, this one would have to be large enough to give an output of hundreds of millions of watts to produce a resonator effect. Moreover, a slight alteration in the speed of the dynamo would throw it "out of tune" with the resonator, so that the effect would disappear. For instance, a 5 per cent. variation of speed would alter the pitch of the dynamo nearly a semitone.

It has been stated that there is a difference of apparent ratio in the Deptford transformer when the main is in circuit; that is to say, that though it generally transforms 4 to 1, when the main is on it tranforms about $4\frac{1}{2}$ or 5 to 1. I would suggest this is impossible. There is always a "drop" in transformers due to waste field. In a transformer for 10,000 volts and 250 amperes, if properly designed, it would be well under 1 per cent., probably about one tenth per cent. In order that an oscillatory current should be confined to the "line" side by the waste induction which causes a drop of 1 per cent. and 80 periods per second, the frequency would have to be enormous. Such an oscillatory current would also be excluded from the secondary at the London end. Any effect which does not involve enormous frequencies must show on both sides of the transformers. It might be said that the "drop" of the transformers in the circuit would give enough self-induction to produce a frequency corresponding to an upper partial of the note of the dynamo. If the dynamo E.M.F. does not vary harmonically, such an effect might be produced, but it would show on the voltmeters at both ends. To give an increase of 15 or 20 per cent. effective pressure, with a total transformer drop of 1 per cent., the frequency would be,

roughly, 1000, and the effective pressure of the oscillatory component 6000 volts. This would give 72 amperes, and the "skin effect" would absorb a great deal of power.

There is, however, a simpler explanation. The cables have considerable capacity, and take an appreciable current. This "leads" relatively to the electromotive force, so the capacity current passes in the armature-coils when they are just in the position to magnetize the fields more strongly. The fields cannot follow each pulsation of excitation so produced, but are affected by it. Their average excitation is increased. I have tried putting a condenser on one of the old Gramme alternators, which have rather weak fields, and a large number of armature ampere turns. The pressure ran up and burned the voltmeter. I have already gone fully into the action of leading and lagging currents on dynamo fields elsewhere, so the subject need not be pursued here. It would, no doubt, be possible to make an alternator excite itself like a series machine by putting a condenser on the terminals instead of exciting the fields by a direct current machine. Such an arrangement seems scarcely commercial, though interesting.

XIII. *On the so-called Meta-Elements.*

By H. M. Vernon, *Scholar of Merton College, Oxford* *.

DURING the last few years we have had brought before us by several eminent chemists, chief among whom may be mentioned Prof. Crookes and M. Lecoq de Boisbaudran, views on the nature of elements totally different from any that had before existed in the minds of chemists. These views being so totally different from anything proposed before, were at first received incredulously, and it is only quite recently that at all a large number of chemists have put faith in them. Even as it is, we may, I think, say that belief in what is referred to, namely the so-called meta-elements, is extremely qualified. The existence of these bodies seems to be so much at variance with the known laws of Chemistry, and especially with that which is known as the Periodic Law, that, though positive proof of their existence would seem to be forthcoming, yet it will probably need much more proof than has at present been advanced to render the belief in their existence universal.

The question now comes, whether these "proofs" of the existence of meta-elements are in reality proofs, or whether

* Communicated by the Author.

they merely point to the possible existence of such bodies. When chemists are called upon to so entirely change their old views upon the constitution of the elements, surely they have a right to expect the most unrefutable proofs why they should do so.

It is with the purpose of examining these proofs for the existence of meta-elements, and of seeing whether they are valid, that this paper has been brought forward.

What is it, then, that we are requested to believe? It is that oxides of certain metals, notably of certain rare earths, are capable, by suitable methods of fractionation and differentiation, of being split up into several other earths, all of which differ from each other and from the original earth, and each of which we are requested to look upon, if not as the oxide of a different element, at least as something approaching to this. That is, we are required to look upon these fractionated earths as oxides of bodies which cannot be formed by the union of other bodies, and which therefore should earn the title of elements.

Let us, then, take an instance of the fractionation of a single earth.

Crookes started with an earth which a few years ago would have been pronounced by every one to be simply yttria, that is, the oxide of the element yttrium. This oxide was dissolved in acid, and enough ammonia added in dilute solution to precipitate only half the base. The precipitate obtained was treated in a similar manner, and so on for several times, the precipitate being collected, dissolved in acid, half of it precipitated again, and so on. The filtrate obtained from the first precipitation was treated in a similar manner. The filtrates and precipitates between these extreme fractions were also made to yield their share to the final products. In this manner, after a very large number of fractional precipitations, a series of earths was obtained which presumably varied gradually in their degree of basicity as they passed from one extreme fraction to the other. In this way Crookes considered he had separated the original yttria into nine new bodies, or oxides of meta-elements, to which he provisionally gave the symbols

$$S_\gamma,\ G_\alpha,\ G_\beta,\ G_\gamma,\ G_\delta,\ G_\epsilon,\ S_\delta,\ G_\zeta,\ G_\eta.$$

In what way, then, was it proved that these nine earths were different?

Some, but not all, of the earths of this class, when sealed up in tubes in which a high degree of exhaustion has been

obtained, and when in this condition subjected to the influence of the induction-discharge, phosphoresce, most of them, it is true, for but a very short time; but with the phosphoroscope contrived by Crookes most of them would phosphoresce long enough to allow of their being satisfactorily examined by means of a spectroscope. Bodies treated in this way are said to undergo the radiant-matter test.

When these nine earths, fractionated from yttria, were sealed up in tubes with a suitable degree of exhaustion, and their phosphorescent spectra obtained in this way, it was found that the spectra of all of them differed to a certain extent. The further the earths were removed from each other in respect of basicity, the more were their phosphorescent spectra found to differ, those of the extreme fractions showing considerable differences.

The differences of phosphorescent spectra appear to be, at least in the case of the yttria earths, the only grounds on which Crookes founds his supposition of the fractionation of this so-called single earth into these nine others. On the strength of the fact of these bodies having slightly different phosphorescent spectra, both when examined alone and, as will be mentioned hereafter, when mixed with other earths, he considers that the earth has been split up into several others, each of which is to be considered the oxide of a different element or meta-element.

The question comes, Do these fractions of the original earth differ in chemical properties as well as in phosphorescent spectra? The answer is, No. The only chemical property in which they appear to differ is that of a slight difference of basicity among themselves. Crookes has not shown that they possess any other chemical properties whatever which may serve to differentiate them from each other; indeed, it appears that he has not yet tried to prepare their salts and show whether or not they are identical.

Again, the question comes, If these bodies do not differ in chemical properties, do they not differ in physical properties other than that of possessing different phosphorescent spectra? Again the answer is, No. Have we not been taught, as one of the fundamental principles of our science, that every different form of matter possesses a spectrum which belongs to it and to it alone? If, then, these so-called meta-elements are different forms of matter, should not they also be expected to come within the precincts of this universal rule? Surely yes. On examination, however, is this the case? In a lecture before the Royal Institution (Chemical News, 1887, p. 87), Crookes brings before the assembly the

spark-spectrum of the original yttria: he then brings before them that of the earth G_η. Are these spectra different? No, absolutely and exactly the same in every particular. He then brings before them that of the earth G_δ. Surely this will be different to a certain degree, even though it be slight. No, it is exactly the same in every respect with the spectra of both the original yttria and of the earth G_η.

How, then, does Crookes explain this? He offers the following alternative suggestions:—

(1) "Elements are not as simple as we suppose. Our notions of a chemical element have expanded. Hitherto the molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the architectural design on which these atoms have been joined. We may consider that the structure of a chemical element is more complicated than has hitherto been supposed. Between the molecules we are accustomed to deal with in chemical reactions and ultimate atoms as first created come smaller molecules or aggregates of physical atoms: these submolecules differ one from the other according to the position they occupied in the yttrium edifice. We may consider them similar to the carbon atoms in the benzene ring which have the impress of their position 1, 2, 3, 4, 5 stamped on them." That is to say, these fractionated earths are to be considered as isomorphous bodies composed of the same atoms arranged in different ways within the molecule. Why, then, call them meta-elements, thereby implying that they contain totally different forms of matter, when in reality they all contain the same?

(2) "These nine earths are chemical elements differing in basic powers and several other chemical and physical properties, but not sufficiently to enable us to effect any but a partial separation. Thus G_δ, for instance, gives a certain spectrum under the influence of the electric spark: the other earths, G_ϵ, G_η, &c., are contaminated with a certain quantity of this G_δ; and so the spectra of these other earths, G_ϵ, G_η, &c., is that of G_δ and G_δ only, they themselves presumably not having any spectra at all, or what they do have is masked by the greater intensity of that of G_δ."

Can this suggestion hold? Is it probable that not the slightest trace of any other lines but those due to an impurity would be observed in the spectrum of a body containing only a small quantity of this other body as an impurity, and not a single one would be observed due to the earth under examination? Surely not.

Again we ask, Do the atomic weights of these fractionated earths differ? Again we must answer in the negative. No

perceptible differences of atomic weight were found between even the extreme members of the fractions.

We therefore come to the conclusion that the entire grounds upon which the fractionation of yttria into several new earths depends is that of the difference of their phosphorescent spectra.

Now it may be asked, Is this radiant-matter test to be absolutely relied upon in every respect with regard to its power of distinguishing between different forms of matter? Does it always give totally different spectra for each form of matter or element as known to us, and does a mixture or compound of two or more elements give the phosphorescent spectrum of each of these elements, or a spectrum different from either?

It appears that Crookes was the first to use, or at any rate to bring into at all general use, this method of obtaining the phosphorescent spectra of bodies when subjected to an induction discharge in an exceedingly rarefied atmosphere. To him therefore we must look for our knowledge of the reliability of this method of examination. He states that the more he makes use of it the more reliable it appears. Do, however, his experiments justify this assumption? The only bodies which he appears to have examined at all completely by this method are these rare earths, and a few other earths of a similar nature, as alumina. Do, then, the results obtained with these bodies justify this method being used to verify such a gigantic innovation as that of the fractionation of the oxide of what was supposed to be a single element into oxides of several other totally new elements? Would the following experiment made by Crookes himself seem to justify it?

In Phil. Trans. 1885, p. 721, Crookes finds that when varying proportions of samaria and yttria are mixed and ignited with sulphuric acid, and tested by the radiant-matter spectroscopic method, a bright orange-line, 2693, is observed, which does not occur in either of their separate spectra, and which disappears as the proportions in which the earths have been mixed approach either to pure samaria or to pure yttria. When, however, yttria and samaria are mechanically mixed and are not treated with sulphuric acid and ignited, only their superposed spectra, without the orange-line, are obtained.

Is not the fact of the bright orange-line being present when the earths are ignited with sulphuric acid, and not being present when they are merely mixed, due to the formation of a compound between the two earths in the first case? It is well known that the spectra of salts which are not decomposed into their constituent elements by the action of heat are

very often quite different from the spectra of the elements composing them. It may be thought that two earths of such similar nature as yttria and samaria are scarcely likely to form a compound together; but yet how else can it be explained? I think if we examine the facts of the case more closely, we shall see that it is not improbable that yttria and samaria should form a compound together. It is well known with what ease the earths of the aluminium group form complex compounds with silica and lime, and may not part at any rate of the minerals, as samarskite and gadolinite, from which these rare earths are obtained, be considered to be in a similar manner complex compounds of the earths?

Crookes has therefore shown that it is possible, by combining two earths together, to obtain a spectrum with a bright line in it which exists in neither of the spectra of the two earths in question: this line has in fact been artificially produced. This being the case, why should it not be possible to manufacture, if we may use the term, other lines and other spectra by the combination of various earths together in varying proportions? Is it not possible that the various spectra of the earths G_α, G_δ, G_η, &c. are nothing more than would be produced if we combined together in various proportions the two, or at most three, earths of which these bodies might be supposed to be really constituted? Do not the experiments of Crookes support this supposition? Thus, about the only property in which these new earths, G_α, G_δ, &c., were found to differ, except as regards their radiant-matter spectra, was that when they were ignited with sulphuric acid and varying proportions of other earths, as lime and barium oxide, they gave phosphorescent spectra in this case also, differing according to the nature and quantity of the base used.

Does not this serve to prove still further the unreliability of the radiant-matter test? If spectra are formed by the union of one of these new earths with lime, say, which differ materially from the spectra of either the earths or the lime, does not this show that no reliance at all can be placed in such spectra, especially with regard to proving that these supposed new earths are really the oxides of new elements. For just as a rare earth mixed with lime gives a spectrum different from that either of the earth or of the lime, so it is just as probable that the earth samaria combined with the earth yttria should give a spectrum different from that either of samaria or of yttria, and also that the spectrum should vary according to the proportions of these two earths present; and it must be remembered that the earth yttria, which has been fractionated into these new earths, always contains a small

quantity of samaria as an impurity, most of this being found in the fraction S_γ: also it is quite possible that a very small quantity of some other earth may be present, and that it may be to the presence of this that the variations in the spectra of the new earths are due. Crookes has shown that the merest trace of a certain earth, unable to be detected by chemical means, can cause great variations in the spectrum of another earth. Perhaps another experiment of Crookes (Chem. News, 1887, p. 87) will serve to still further confirm the point at issue, namely, the unreliability of the radiant-matter test.

Marignac presented Crookes with what was supposed to be a pure specimen of a new earth, to which he had provisionally given the symbol $Y\alpha$. This earth was found to possess a radiant-matter spectrum almost identical with that given by a mixture of 61 parts of yttria and 39 parts of samaria, which had been ignited with sulphuric acid. The only difference was that in the yttria-samaria spectrum there is present a citron band which is absent from the $Y\alpha$-spectrum. "Hence the earth $Y\alpha$ is shown to consist of samaria with the greenish blue of yttria, and some of the other yttria bands added to it. It proves further that the citron band, which was hitherto regarded as one of the essential bands of the yttria spectrum, can be entirely removed, whilst another characteristic yttrium group, the double green band, can remain with heightened brilliancy. If, now, it were possible to remove the citron-band-forming body from this mixture, the earth $Y\alpha$ would be left behind; in fact, the earth $Y\alpha$ would have been recomposed from its elements." This, Crookes says, he has no doubt he will ultimately accomplish.

Now the earth $Y\alpha$ must either be identical with the yttria-samaria earth, or it must be distinct from it. If it is identical, then the radiant-matter test is not reliable, as the same bodies have been found to give spectra which do not coincide in all their lines. If it is distinct from it, then the radiant-matter test is equally unreliable, as different bodies have been found to give spectra the larger portions of which are absolutely identical.

It has thus been shown how very little reliance can be placed in this new physical method of differentiating bodies. Time alone will show the degree of reliance that should be placed in it. Even Crookes himself seems to feel this in some parts of his papers, though in others he states that the further he goes the more reliable he finds it to become. In Phil. Trans. 1885, p. 722, he says:—"One important lesson taught by the many anomalies unearthed in these

researches is that inferences drawn from spectrum analysis *per se* are liable to grave doubt, unless at every step the spectroscopist goes hand in hand with the chemist. Spectroscopy may give valuable indications, but Chemistry must after all be the final court of appeal."

I think it has been shown that, at least in the case of the yttria earths, Chemistry has not been made the final court of appeal, or if it has it has signally failed to prove its case.

The existence of meta-elements has been sought to be established indirectly in ways other than that of the fractionation of the rare earths. Thus A. E. Nordenskiöld (*Comptes Rendus*, November 2nd, 1886) finds that the earth gadolinia, which consists of a mixture of yttria, erbia, and ytterbia, has. though palpably a compound body, a constant atomic weight whatever be the mineral from which it has been extracted. "Therefore," says he, "oxide of gadolinium, though it is not the oxide of a simple body but a mixture of three isomorphous oxides (even when it is derived from totally different minerals found in localities far apart from each other), possesses a constant atomic weight. We are then in the presence of a fact altogether new in Chemistry; for the first time we are confronted with the fact that three isomorphous substances, of a kind that chemists are still compelled to regard as elements, occur in nature not only always together but in the same proportions."

This may be explained by saying that these three earths form a compound together, just as we form compounds of alumina with silica and lime or magnesia in the form of complicated silicates, which, being chemical compounds, have a constant composition whatever be the locality from which they are obtained. Surely Nordenskiöld does not mean to state that none of the earths yttria, erbia, or ytterbia ever occur except together, and that too in perfectly constant proportions? Has not Crookes quite recently shown that yttrium is one of the most widely distributed of elements? He does not mention that erbia and ytterbia also always occur together with this yttria, and that too always in the same proportions. Also, do not minerals as samarskite contain many other earths besides the three in question?

It has thus been shown that the resolution of yttria into several other new earths has by no means been proved. May we not reasonably expect that as further investigation is made in the subject it will be found that these different radiant-matter spectra are only due to the combinations of two or perhaps three earths already known and recognized as oxides of

distinct elements, and that all that fractionation actually does accomplish is to partially separate these two or three earths, which very much resemble each other in most of their properties, and which are therefore confounded together.

But, it may be said, even if this be found to be the case, will not the number of distinct earths be so large that it will not be possible to find places for them in the table of elements, arranged according to the Periodic Law, and even then is it possible to explain why such a large number of elements should exist, apparently differing in very little besides their atomic weights and basicity?

On examination, I think it will be found that not only is there a place in the table of elements arranged according to the Periodic Law for all of the rare earths at present discovered, but for several more besides; and also that a reasonable explanation can be offered why so many of these elements, so similar in almost every property, should exist.

The members of these rare earths which have been discovered during the last few years are as follows:—

Lanthanum	138	Terbium	124·7
Cerium	140·2	Erbium	166
Didymium	142·3	Ytterbium	173·7
Samarium	150	Thulium	169·5
Mosandrium	153·6	Scandium	44·1
Holmium	162	Yttrium	89·1

Several other new elements of this class, besides those mentioned here, have been claimed to have been discovered, but their existence is so exceedingly doubtful that they have not been introduced in this list. Also two or three of those here mentioned have but a very doubtful existence. The numbers attached to these elements are their atomic weights, calculated on the assumption that the earths analysed had a composition expressed by the formula R_2O_3.

The two constituents neodymium and praseodymium into which Dr. Auer von Welsbach has separated didymium into are not mentioned in this list, as it was thought better to wait for confirmation of this remarkable result by other chemists.

Let us now take each of these elements separately and see if there is a place for it in the table of elements.

In this table two series of elements have been introduced between the series commencing with cæsium and that commencing with gold, as suggested by Brauner (Chem. Soc. Journ. 1882, p. 78).

	1.	2.	3.	4.	5.	6.	7.	8.
1.	H 1							
2.	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3.	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·5	
4.	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56; Ni 58·6; Co 59.
5.	C 63	Zn 65	Ga 70	Ge 72	As 75	Se 78	Br 80	
6.	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	.....	Ru 103; Rh 104; Pd 106.
7.	Ag 108	Cd 112	In 113	Sn 117	Sb 120	Te 125	I 127	
8.	Cs 132·7	Ba 137	La 138	Ce 140	Di 142	145	149	Sm 150; Ms 153·6.
9.	156	160	Ho 102	Tb 165	Er 166	167	169	
10.	170	172	Yb 173·7	178	Ta 182	W 184	189	Os 191; Ir 192·5; Pt 194.
11.	Au 196	Mg 200	Tl 204	Pb 207	Bi 208			
12.	.....	.....	.....	Th 232	.....	U 240		

The reason of this is that the extra elements in the eighth group are only found attached to the even series 4 and 6; if only one series were introduced between those commencing with cæsium and gold, then the extra elements osmium, iridium, and platinum in the eighth group would come in an uneven series. Also, if only one series were introduced, the difference between the atomic weights of cæsium and gold would be 63·3, which is not nearly so similar to the difference between the atomic weights of cæsium and rubidium, which is 47·7, as that between cæsium and copper, which is 69·7. Also still further reasons will be shown to exist why this extra series should be introduced.

Of the elements in the list, lanthanum, cerium, and didymium without doubt take their places in the eighth series in the third, fourth, and fifth groups respectively. The next two elements in order of atomic weight are samarium (150) and mosandrium (153·6): Where must these two elements be placed? Their atomic weights compel them to be placed in this series, and they evidently cannot be placed in the sixth and seventh groups. They must therefore find their place in the eighth or extra group. There seems to be no reason why they should not; for the elements iron, nickel, and cobalt form compounds of the form R_2O_3, and indeed the stablest compounds of iron are grouped under this formula. Also the elements composing these minor groups in the eighth group resemble each other very greatly in almost all their properties; in the same way does samarium resemble mosandrium in its properties; and when another element of the atomic weight 151 is discovered to fill up the gap between these two elements, as will very probably be the case, there is every reason to expect that it will show very great analogies to the other two elements in the same minor group as itself. If these elements, samarium and mosandrium, had not been discovered, their existence might readily have been predicted, as a minor group of elements in this eighth group belonging to the eighth series is so evidently needed to bring this series into harmony with the fourth, sixth, and tenth. We see in this also additional evidence for the introduction of two series between these commencing with cæsium and gold.

The next element on the list is holmium, the place for which in the table is evidently the third group in the ninth series.

Next comes the element terbium, the atomic weight of which was found to be 124·7 on the supposition of its oxide having the formula Tb_2O_3. We see that there is no place for

this element in the table if its atomic weight be taken as this number. If, however, it be considered a tetravalent element, its atomic weight becomes 165, and it fits in well in the fourth group of the ninth series. It is very probable that terbium should be a tetravalent element forming salts of the formula Tb_2X_4; for cerium, the commonly occurring oxide of which is Ce_2O_3, is well known to form these salts, and terbium is very similar in properties to this element.

The next element, erbium (166), finds its place in the fifth group of this series, whilst the next, ytterbium (173·7), is placed beneath lanthanum and holmium in the third group of the tenth series. The only element in the list for which a vacant place does not appear is thulium (170·7); very little if anything is known of the properties of this element, and so it is scarcely possible to say which group it had better be placed in: it does not appear as if it would fit any of the places in the table at present empty, and so, if further research tends to confirm its being a trivalent element with this atomic weight, it will certainly constitute a difficulty not to be lightly got over.

We have thus found, with perhaps one doubtful exception, that there are places in the table of elements for all the rare earths discovered up to the present time, and, moreover, that these places agree well with such properties of these elements as are at present known. It may also be noticed that there are several empty places ready to receive any more newly-discovered elements.

The conclusion which may be drawn from the results arrived at in this paper are, that it would seem quite unnecessary to suppose the actual decomposition of what was previously supposed to be an element takes place when an earth is fractionated in some suitable manner as by partial precipitation. If such a decomposition is possible for one or two elements, we may reasonably expect it for all. Why, then, is it not attempted to fractionally separate an element which can be obtained in a pure state to start with? In the fractionation of these earths, it is almost if not quite impossible to obtain the earth in a pure state in the first instance; that is, to obtain an earth which is known not to contain at least a small quantity of some other earth totally foreign to it (disregarding the several so-called meta-elements into which it is to be separated). The difficulty is also enormously complicated by the fact of the earths which are attempted to be fractionally separated having almost exactly the same properties as at least half a dozen other earths.

If it is an earth which is required, why not endeavour to fractionate alumina, an earth which, though resembling other earths of its class, to a certain extent is yet in many of its properties totally distinct from them? Again, if it is thought possible, were suitable means known to fractionate any element, why not endeavour to do so in the case of iodine? This element, being situated at the extreme end of its series, differs as much as it could possibly do from cæsium, the element next to it in order of atomic weights. If, therefore, it were possible to separate iodine into bodies with atomic weights approaching gradually to that of cæsium, might it not be thought that a very slight difference of atomic weight would correspond to a very much larger variation in chemical properties?

The actual fact of there being such a large number of these rare earths so very similar in properties is to be partly explained by the fact that not only these elements, but also the other members composing the table, show extreme variations among themselves to a smaller and smaller extent as their atomic weights get larger and larger. Also all these elements, except samarium and mosandrium, find their places in the third, fourth, and fifth groups, and are on this account naturally to a certain extent similar in properties.

It is hoped that in this paper the views and actual results of any chemist have not been misinterpreted. It has been endeavoured as far as possible to be correct, but if any slight errors have been committed, it is hoped that they will be recognized as being unintentional.

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Oxford.

XIV. *On the Use of Fluor-Spar in Optical Instruments.* *By* Professor Silvanus P. Thompson, *D.Sc., &c.**

CONSIDERING the very distinctive optical properties of fluor-spar, it is remarkable that hitherto so little use has been made of it in the optical industries. Its low refractive power, and its still lower relative dispersion, make it remarkable amongst transparent media; the only substances comparable with it in these respects being rock-salt and rock-alum, both of which being soluble in water are for that reason

* Communicated by the Author, having been read before Section A of the British Association at Leeds.

unfitted for use in optical instruments. Like these substances also, fluor-spar is optically isotropic, belonging to the cubic system of crystals.

The crystals of fluor-spar most usually occurrent in this country are by no means colourless, being generally purplish in tint, and exhibiting at the surface nearest to the light a fine fluorescence. Another variety, known as chlorophane, is of a pale green tint. Pure colourless crystals have also been found in Cornwall and in Switzerland; but these are now rather rare.

Lenses and prisms of fluor-spar have been from time to time used, instead of those made of rock-salt, for experiments on radiant heat; and, indeed, until recently this was the only optical application of this material.

Recently, however, fresh attention has been drawn to the subject by the announcement from the pen of Prof. Abbe, of Jena, that it is by the use of fluor-spar in combination with various sorts of glass that the well-known firm of Zeiss have been enabled to construct the remarkable microscope-objectives known as "apochromatic" lenses. These lenses were for long supposed—in spite of much scepticism on the part of opticians—to owe their excellent resolving power to the use of the new kinds of optical glass produced in Jena by Dr Schott. The secret, which was remarkably well kept for several years, is now revealed. Triplet lenses, somewhat like a Steinheil lens, with a fluor cemented between two outer lenses of glass, are used to correct the aberrations of the front lenses of glass. The peculiar value of the fluor lens for this purpose lies in its possession, alluded to above, of a singularly low dispersive power. According to Abbe the refractive index of the colourless fluor for sodium light is 1·4338, and for the hydrogen lines C and F the respective indices differ only by 0·00455. For the sake of comparison with other materials, it is convenient (following Abbe) to consider the quantity

$$\frac{\mu_F - \mu_C}{\mu_D - 1}$$

as a measure of the specific power of any material to produce dispersion. Now, for ordinary crown-glasses, this quantity is about 0·0166; for dense flint as much as 0·019; for the special phosphate crown-glasses made at Jena it is as low as 0·0143; while for fluor-spar it is only 0·0104. As Abbe points out, the possession of this property enables the instrument-maker, by substituting fluor for crown-glass, to produce

an achromatic lens, consisting of flint glass and fluor-spar, having faces of lesser curvature than would be requisite for a lens made of crown-glass with the same sort of flint. This is obviously a great advantage, as both the spherical aberration and the chromatic differences of the spherical aberration are reduced when the curvatures are lessened. Hence the use of fluor-spar for the construction of the improved achromatic lenses may be regarded as an application of this material of considerable importance.

I have now the honour of announcing a third application of fluor-spar; namely to the construction of direct-vision prisms for spectroscopic purposes. The very same considerations which render fluor superior to crown-glass for achromatizing lenses render it, by an inverse use of the material, superior to crown-glass for the purpose of procuring, along with prisms of dense flint, a wide dispersion. A direct-vision prism made of one wide-angled prism of dense flint-glass between two prisms of fluor has as great a dispersion-power as an ordinary five-prism combination of alternate crowns and flints. Such a prism, constructed for me by Mr. C. D. Ahrens, a few months ago, shows extremely good definition. It is of course shorter than an ordinary crown-flint combination of equal power, and requires fewer surfaces to be worked optically true.

When talking over this prism with Mr. Ahrens, he made the remark that it would now be possible to construct a direct-vision prism wholly without glass. This suggestion has since borne fruit; and enables me to present to the Section a small piece of apparatus which I believe is an entire optical novelty, namely a spectroscope which also polarizes the light. It consists simply of three prisms cemented together, like an ordinary direct-vision prism; the two end prisms being of fluor-spar, and the middle prism of Iceland spar. The latter is cut (as in the improved Nicol prisms which I have on two former occasions described at meetings of the British Association) so that the crystallographic axis of the spar lies at right angles to the line of vision. The combination, which was constructed by Mr. Ahrens, acts therefore both as a Nicol prism and as a direct-vision prism. It is intended to be employed in spectrophotometric measurements.

For the purpose of direct-vision prisms the fluor-spar employed must be of the colourless kind, as a considerable thickness of it is necessarily interposed in the path of the light. That which Mr. Ahrens has cut for me is almost colourless, having a feeble green tinge. The combined prism

of fluor and Iceland spar is far less absorbent than the direct-vision prisms ordinarily made with dense flint glass of a strong yellow tinge. For the purpose of achromatizing lenses the presence of a greenish or purplish tinge is of less importance, as a smaller thickness is used : and the purple fluorescence, which is objectionable in some ways, will not trouble the performance of the lens for any but photographic service.

It is of importance to note that the tint, whether purplish or greenish, of fluor-spar may be greatly reduced or nearly removed by simply heating the spar to a temperature a little above that at which it emits light in a darkened room. Care is necessary, however, that the crystals should not be heated either so suddenly or to so high a temperature as to cause decrepitation. Another point of even greater importance in the optical applications of fluor-spar is the selection of crystals which are not macled. Macled crystals of fluor seldom fail to show, when cut, some trace of double refraction which would unfit them for optical purposes.

The refractive index of the pale green variety seems to be a little higher than that of the colourless spar. I find 1·435 as the sodium-light index of refraction, as against 1·4338 found by Dr. Abbe.

City and Guilds Technical College,
Finsbury, September 3, 1890.

XV. *On the Alternating Electric Arc between a Ball and Point.* *By* Edward L. Nichols*.

Part I.†

THE phenomenon which forms the subject of this paper was first brought to my notice by Mr. E. G. Acheson, the result of whose unpublished observation may be briefly stated as follows :—

Two wires, which formed the terminals of the secondary coil of an alternating-current transformer, were brought nearly into contact. One wire was armed with a ball, the other with a point. When the distance was such as to admit of a discharge between the two, it was found that a galvanometer in shunt around the ball and point indicated a considerable flow of continuous current.

This phenomenon has recently been subjected to investiga-

* From Silliman's American Journal of Science, January 1891.

† From experiments made by Messrs. W. K. Archbold and G. L. Teeple.

tion by Messrs. Archbold and Teeple. Their experiments, from which in great measure the data used in the first part of this paper have been taken, are described at length in their Thesis in Electrical Engineering, which is now in the library of Cornell University*.

The apparatus used in the verification of Mr. Acheson's observation consisted of a Ruhmkorff-coil of moderate size, the interrupter and condenser of which had been thrown out of circuit. The primary coil, as in all instruments of that type, consisted of a few turns of heavy wire surrounding a core of iron wires. When this coil was supplied with current from a small alternating-current dynamo, making 14,000 reversals a minute, and the terminals of the secondary coil were brought into position, a discharge of considerable brilliancy took place between them. To the unaided eye the discharge appeared to be perfectly continuous; but the fact that it was really of an intermittent and periodic character was indicated by the emission of a well-defined musical note, which corresponded in frequency with the period of alternation of the dynamo.

The terminals of the secondary coil were subsequently connected with a brass ball about one centimetre in diameter, and with a point consisting of a steel sewing-needle. These were mounted horizontally in well-insulated bearings, the centre of the ball in line with the axis of the needle. The distance between the ball and the point of the needle was capable of adjustment by means of a micrometer-screw. A mirror-galvanometer of two thousand ohms, having in its outer circuit about one hundred thousand ohms, was shunted around the ball and point (in parallel circuit with the air-space between them). When the induction-coil was put into operation, the ball and point being too far apart to admit of a visible discharge, the galvanometer-needle remained at zero, but when they were brought within striking distance a large and constant deflexion was produced. When the ball and point were interchanged the deflexion was reversed, its direction always being that which would have resulted from a current flowing from the ball to the point. Under the influence of the discharge, which was intensely luminous, the steel needle was fused at the point and rapidly wasted by oxidation, so that it became necessary to find some more

* 'The Effect of placing a Ball and Point in a High Potential Alternating Current Circuit,' by W. K. Archbold and G. L. Teeple. Thesis in MS., Cornell University Library, 1889.

refractory material*. It was finally supplanted by a pointed platinum wire, which, although rendered highly incandescent, withstood the temperature of the arc much better than steel had done.

The following quotation will serve to indicate the conclusions reached by the observers in the course of their preliminary experiments with the platinum point :—

"The behaviour of the arc as its length is increased is very curious. As the point is withdrawn the arc forms and sings with an even tone, the pitch corresponding to the number of alternations. The point becomes of a dull red colour, while the galvanometer gives a small but quite steady deflexion. As the arc is drawn out it sings louder and more harshly, the point becomes redder, while the galvanometer deflexion increases and becomes very unsteady. At a certain critical length the following phenomena suddenly occur:—the tone becomes smooth and even, the point brightens almost to a white heat, the intensity depending upon the strength of the current, while the galvanometer deflexion becomes much greater and very steady. The explanation suggested, and which subsequent experiments seem to confirm, is as follows:—At first the arc forms both ways, the rapid succession giving the tone. As the arc lengthens the arc still forms from ball to point, but is only intermittent (occasional) from point to ball, giving the unsteady tone and deflexion. Finally, the distance becomes too great for the arc to form from the point to the ball, while it still passes freely the other way, and the tone and deflexion become steady" †.

It was to the conditions existing in the circuit when the critical length of the arc, above mentioned, had been reached, that Messrs. Archbold and Teeple chiefly devoted themselves. The limits between which it was necessary to maintain the arc were exceedingly narrow, a very slight extension of the striking distance beyond the critical point resulting in total extinction of the discharge. Small changes in the speed of the machine

* The attempt to use carbon terminals led to the following observation :—"A carbon pencil substituted for the point gave the same effect, but upon putting the carbon in place of the ball it still acted as a 'point.' If two carbons were used the more pointed one acted as a 'point.' (It was observed that the end of the needle was fused into a ball by the heat of the arc, and would then act as a 'ball' to the smaller particles of carbon projecting from the end of the pencil.) Two brass balls brought together caused a drifting of the galvanometer-needle from one side to the other, according, it is to be presumed, as the discharge changed the nature of the two surfaces, so that minute points formed on one or the other." (Archbold and Teeple, Thesis, p. 3.)

† Archbold and Teeple, Thesis, p. 5.

were sufficient to throw the apparatus out of adjustment, and the arc, once ruptured, would not reappear spontaneously. It could be re-established, however, by the momentary introduction of a bit of metal between the ball and point, or even by the interposition of a candle-flame. The complete stability of the discharge was finally secured by driving the dynamo by means of a motor, the latter being supplied from a storage battery.

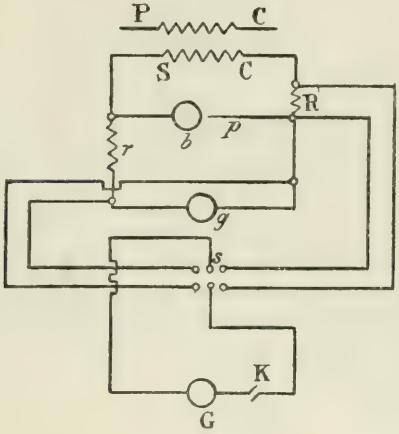
The main portion of the investigation consisted in the determination of the periodic changes of electromotive force and current during a complete cycle, when no arc existed, and of the modifications introduced into the curves of potential and current by the discharge between ball and point. Throughout the entire series of measurements, the striking-distance was greater than the critical values already defined, a condition the maintenance of which was secured by watching the indications of the galvanometer.

The instrument used in the measurement of electromotive force was a Thomson mirror-galvanometer of ten thousand ohms resistance. The galvanometer line was carried to the dynamo, where, by means of an instantaneous contact device, the circuit was closed during an interval of exceedingly short duration, once in every revolution. The device consisted of a wooden disk, mounted upon the shaft of the machine. A single bar of brass, on the periphery of the disk, passed under a brush at every turn. This bar was connected metallically with a brass collar on the shaft, and a second brush bearing upon the collar completed the circuit. By thus closing the line through the galvanometer, for an instant, once in a revolution, the electromotive force of the second circuit, at that particular point of the cycle for which the contacts were made, could be measured; and since the brush was adjustable through considerable range, the entire cycle could be explored.

The arrangement of the entire apparatus is shown in fig. 1. PC and SC are the primary and secondary coils of the inductorium, p and b are respectively the point and ball. R is a non-inductive resistance, g the indicating galvanometer, in parallel with the ball and point, r a non-inductive resistance, s a switch by means of which the Thomson galvanometer could be shunted at will around R or g. K is the instantaneous contact-device, and G is the Thomson galvanometer. When the Thomson galvanometer was shunted around R, which was placed in the main circuit leading from the induction-coil, it served to indicate the current flowing in that circuit during that portion of the cycle for which contact was being made; when connected in shunt with the gal-

vanometer g, it measured the fall of potential through the coils of the latter instrument. The function of the indicating

Fig. 1.

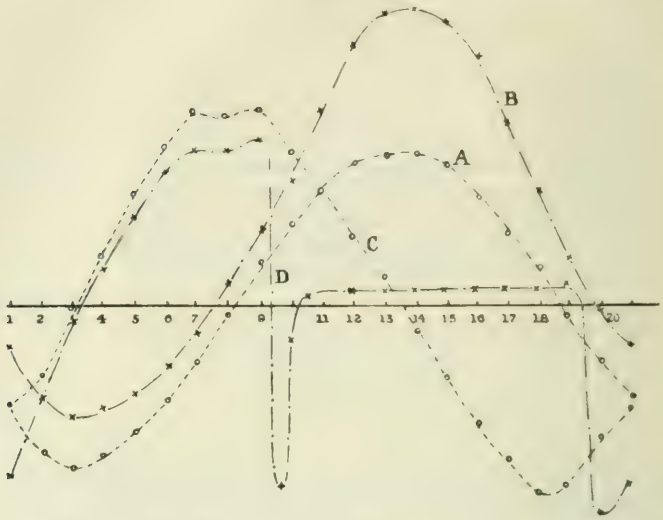


galvanometer, during this part of the investigation, consisted in showing, by the size and direction of its deflexion, whether the discharge between the ball and point continued to maintain its proper character.

The result of measurements throughout a complete cycle, both when the arc was formed and when it was extinguished, is shown in curves B and A (fig. 2). Curve A is with close approximation a curve of sines, and it indicates the usual fluctuations of current to be looked for in the secondary circuit of an alternating system. Curve B shows the current throughout the cycle when the arc was playing. Abscissæ represent portions of a complete cycle, the period being divided into twenty equal parts, ordinates the relative amounts of current through the resistance R, or the total current in the secondary circuit. Deflexions, when the current flows from ball to point, are plotted above the base line. As may be seen from the curve B, the current flowing in the positive direction during each cycle was greatly in excess of that flowing in the negative direction, when the discharge was taking place between ball and point, whereas when no arc was formed (curve A) the areas inclosed by the positive and negative branches of the curve were equal. Now there were two paths offered to the current, that through the galvanometer g and the resistance r, which consisted of a column of copper-sulphate solution

between copper poles (approximately 112,000 ohms), on the one hand, and the parallel circuit between the ball and point on the other. The resistance of the latter path was infinite

Fig. 2.

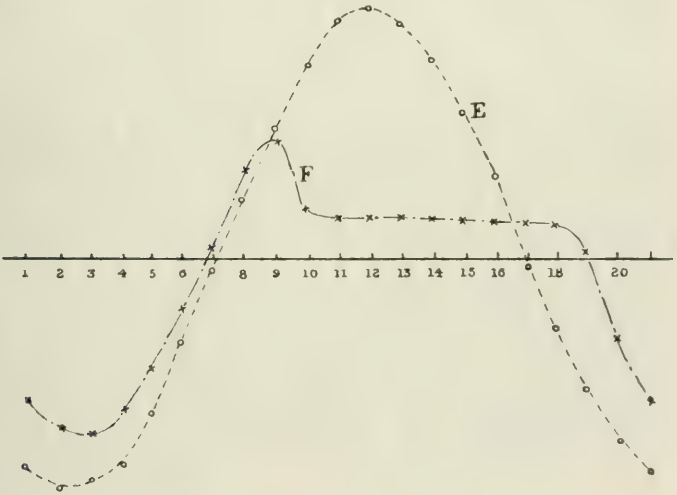


whenever the arc was interrupted, falling to finite values during each discharge. Increase of current through R indicates, therefore, the formation of the arc. Such increase is found to exist during the second half of each cycle, that is to say, during that interval in which the ball is positive ; and it might be inferred from these curves alone that the discharge was an intermittent one taking place always from ball to point. Other curves, taken simultaneously with A and B, the Thomson galvanometer being shunted around the indicator galvanometer, lead to the same conclusion. The curves marked C and D (fig. 2) show the results obtained. It was thought that they would give the fluctuations in electromotive force between ball and point, corresponding in time to the current fluctuations in the resistance R. The indicating galvanometer, however, owing to the very rapid alternations to which the circuit was subjected, was found to possess such high self-induction as to materially influence the result. Strictly speaking, the curves C and D, therefore, give the periodic changes of electromotive force at the terminals of the indicator and not those occurring at the ball and point.

These curves are nevertheless of considerable interest. The

curve C shows the character of the cycle when no arc was formed, and D, when the arc was in operation; C, like A, is approximately a curve of sines. The irregularity at its positive crest, which also appears in D, is probably due to the imperfect performance of the contact brush, and, having no bearing upon the phenomena which the curves are intended to elucidate, may be disregarded. Since no current was passing between the ball and point when A and C were taken, they represent the fluctuations in successive portions of the same circuit. The lag, due to self-induction, however, is very marked, amounting to almost 90° of phase. Curve D, which shows the influence of the arc, is especially instructive. The potential rises during the first part of the cycle (ball positive); then follows a very sharp oscillation, occupying about one twentieth of the entire period or 1/4600 of a second of time. The potential then reaches a small positive value, which it maintains without fluctuation for at least four tenths of a complete cycle, when it suddenly becomes strongly negative.

Fig. 3.



To obtain curves of electromotive force between ball and point directly, a non-inductive resistance was substituted for the indicating galvanometer, and the measurements from which curves C and D had been drawn were repeated. Of the two curves thus determined, the one taken when the arc was not playing (E, fig. 3) is a sine curve closely coinciding in phase

with the simultaneous curve of current (A, fig. 2). The corresponding curve F, which was taken while the discharge was passing between the ball and point, is in its essential features of the same character as curve D (fig. 2). The interval of uniform positive potential is of the same length, and it is coincident with the interval of excess of current which shows itself in the positive branch of curve B. It is noteworthy that this interval of uniform potential which marks the duration of the arc, occupies in both cases the same portion of the cycle (between scale-divisions 10 and 19, approximately), although there is otherwise a difference of phase, due to self-induction, amounting to at least four scale-divisions. Curve C, for instance, reaches its maximum in the neighbourhood of scale-division 8, curve E at scale-division 12. The exclusion of the coils of the indicating galvanometer from the circuit reduced this difference of phase to a small quantity, and it suppressed altogether the remarkable oscillation of electromotive force (see curve D) which in all preceding experiments had introduced the formation of the arc.

The results exhibited graphically in these six curves afford abundant verification of the theory of the ball and point phenomenon, given in a previous paragraph; and they establish the fact that in the secondary circuit of a transformer, such as that made use of in these experiments, the striking-distance from ball to point exceeds that from point to ball. It follows that whenever the space between the ball and point is less than the former and greater than the latter distance, discharge will occur only during that portion of each alternation for which the ball is positive, and that under such circumstances a galvanometer placed in the circuit will show a constant deflexion.

Complete corroboration of the foregoing conclusion was obtained by studying the image of the arc in a revolving mirror. With an arc of less than the critical length the discharge was seen to consist of two distinct sets of sparks, all of the same duration but differing in colour. Each alternate discharge was purple, the intermediate ones being of a greenish cast. The spark-images were everywhere equidistant, and their duration was about four times as great as the intervening intervals of darkness. The extension of the sparking-distance beyond the critical point resulted in the complete suppression of the series of purple images, the intermediate ones remaining undisturbed in position, duration, and appearance. The intervals of darkness were then estimated to occupy six tenths of each cycle, the discharges four tenths; a ratio which corresponds with that of the duration of positive poten-

tial of the ball (as shown in the curve) to the total length of a complete cycle.

The ball-and-point phenomenon is unquestionably very closely related to a class of effects with which students of static electricity have long been acquainted. One recalls, to begin with, Faraday's experiments with the Leyden jar; in which, of two paths, the spark invariably followed that involving passage from a positive ball to a negative point, in preference to another, through equal air-space between a negative ball and a positive point*. Wiedemann and Rühlmann have since shown that, between spherical electrodes which differ in diameter, the quantity of electricity necessary to produce a discharge is less when the larger ball is positive than when it is negative†; and Macfarlane has measured the electromotive force which will produce a spark between a point and plate, and has found it to be greater when the point is positive than when it is negative‡.

In view of the experiments described in the present paper, it appears that what is true, in this particular, of the spark from the Leyden jar and the discharge of the Holtz machine, is true also of the alternating-current arc.

Part II.§

After the completion of the experiments of Messrs. Archbold and Teeple, the study of the Ball-and-Point Phenomenon was taken up under the writer's direction by Mr. F. C. Caldwell; the chief purpose of the investigation being to test the applicability of the effect to alternate current measurement ‖.

Irregularities of action due to rapid changes in the surfaces of the point and ball, by corrosion and disintegration under the arc, finally caused the attempt to be abandoned for the time being, but Mr. Caldwell in the course of his work made a large number of observations of the discharge under various conditions. Many of these are of interest in this connexion on account of the light which they throw upon the original experiments, and because of the lines of further research which they suggest.

* Faraday, Experimental Researches, § 1493.

† Wiedemann and Rühlmann, *Annalen der Physik und Chemie*, cxlv. See also Wiedemann, *Elektricität*, iv. p. 462.

‡ Alexander Macfarlane, Proceedings of the Royal Society of Edinburgh, vol. x. p. 555 (1879–80).

§ From experiments made by Mr. F. C. Caldwell.

‖ Frank Cary Caldwell, "A study of the Alternating Arc between a Ball and Point." Thesis in MS. Library of Cornell University (1890).

Mr. Caldwell's first step, after having repeated the preliminary experiments of Archbold and Teeple, and verified their statements, was to substitute a ball with a surface of platinum for the brass ball used by them. The new ball withstood the action of the arc no better than the old one had done. It soon became covered with a black deposit, the growth of which modified and vitiated the action of the apparatus. In experimenting with such a ball, the surface of which was still bright and new, and with a point of the same metal, it was noticed that within the critical distance, while the spark was passing in both directions, there appeared to be two distinct paths along which the discharge was taking place. One of these was nearly in the line from the point to the ball, normal to the surface of the latter, the other from the point in a direction approximately at 45° with the common axis of the pointed rod and ball. Upon increasing the distance until the discharge entered the "one way" stage, the longer and oblique path of flow vanished. In the revolving mirror the two classes of sparks were easily identified. They were found to occur in alternation with each other, the spark which followed the normal path being that which passed from ball to point, the other that from point to ball. The images of the discharge from the point disappeared as soon as the critical distance was reached. In order to place the matter beyond all doubt, the times of the discharge which followed the normal path were determined by an ingenious method, quite independent of that used by the first observers, and it was found that the spark occurred always in that part of the cycle during which the ball was positive.

Mr. Caldwell's method of fixing the time of the discharge, briefly stated, was as follows. An adjustable contact device, similar to that used by Archbold and Teeble, was attached to the shaft of the dynamo. A wire from one pole of a large Holtz machine, driven by power, was carried to the neighbourhood of the ball and point, where two platinum terminals, 1 millim. apart, were set up. The wire was connected with one of these, and a line was carried from the other to the contact device. A wire from the latter to the remaining terminal of the Holtz machine completed the circuit. Whenever the brush made contact, a spark leaped between the platinum terminals just described. By adjustment of the brush, the spark could be made to appear at any desired instant in the cycle of alternations of the dynamo. The platinum terminals were placed so that the image of the spark in the revolving mirror was seen side by side with that of the discharge

between the ball and point, and the precise position in the cycle occupied by the latter was thus readily determined.

Closer study of the two paths of discharge showed that the oblique arc left the very apex of the point, swinging out laterally into its path ; also that the normal arc, on approaching the point, avoided the apex and entered the wire from the side, never passing in at the point itself.

From these observations it appears :—

1. That the discharge from the ball (positive) leaves the latter in a direction normal to the surface, but that it enters the other terminal at some distance from the apex.

2. That the discharge from the point (positive) leaves the very apex of the latter, but is deflected into a course nearly 45° from the axis and reaches the ball obliquely at some point on its side.

Taking these observations into consideration, the explanation of the cessation of the discharge from the point at the critical distance and of the establishment of the "one way" arc, follows at once. The two paths of discharge differ in length, and for a given electromotive force the maximum striking distance is sooner reached in the case of the oblique than of the normal arc, so that the latter continues to pass at greater distances (of ball and point) than the former.

Further inspection of the images of the two arcs in the revolving mirror revealed another curious fact. The mirror was set up with its axis of revolution parallel to the common axis of the ball and point. The image of an instantaneous spark following the line of the normal arc would therefore be a line parallel to the axis of the mirror. Since the duration of the discharge was nearly ·001 second, this linear image was expanded into a broad rectangular band. The image of any oblique discharge would in general be an oblique parallelogram. The image of the discharge from point to ball, however, was not of that form. It appeared rather as a warped surface the form of which could be explained only by supposing that the discharge at first followed the normal path to the ball, and was gradually displaced as the cycle progressed, until it reached its extreme position at 45° to the axis, just before the rupture of the arc.

Definite results were obtained only while the platinum surface was new and bright. The region where the normal arc left the ball soon became tarnished and corroded and there was an increasing tendency on the part of the oblique arc to leave its own path and join the other.

When the ball was supplanted by a platinum wire, 1 millim.

in diameter, with rounded tip, the object being to force the two discharges into a common path, it was found that the arc from the point (positive) avoided the end of the wire altogether, and struck in upon the cylindrical surface beyond. When the end of this wire was surrounded by an insulated platinum ring which was connected with the terminal of the induction-coil by a separate wire—the intention being if possible to separate the two phases of current and conduct them over different wires—it was found that the arc from the point (positive) always entered the centre wire, never being diverted to the ring, although the intervening air-space was less than a millimetre. The returning arc, however, would sometimes leave the ring and sometimes the wire, and a galvanometer placed in the circuit between the ring and the induction-coil showed a large deflexion, such as would be caused by a flow of current towards the ring. This result seems to be in accordance with the conclusion reached from the inspection of the images in the revolving mirror; namely that the arc from the point always formed first along the shortest path. Deflexion from that path in the case of the wire and ring would probably be hindered by the insulating medium which intervened. When, finally, a cluster of points were opposed to the single point, it was found that the discharge from the latter was always along a single path, whereas the return arc from the cluster (positive) often followed several paths.

It had been noted by Messrs. Archbold and Teeple, that the platinum point used in their experiments, which was red-hot while the arc was passing in both directions, became white-hot during the "one way" stage. The heating-effects at the surface of the brass ball were not discernible, but when Mr. Caldwell substituted a thin sheet of platinum for the ball, this became incandescent under the action of the arcs. The spot where the oblique arc (point positive) impinged upon the foil became white-hot, while that at which the normal arc (ball positive) left the foil was barely red-hot. In this respect, then, the discharges act like the ordinary sparks of the influence-machine or induction-coil, which, as has been shown by Despretz, Poggendorf, Naccari, and other observers, heat the negative electrode to a higher degree than the positive one. This action is in marked contradistinction to that of the continuous current arc, the positive terminal of which takes the higher temperature.

In this brief account of Mr. Caldwell's experiments, I have omitted to mention many of the observations recorded by him. He had occasion in the course of his investigation to study

the discharge under a variety of conditions, and found that when liquid surfaces (mercury or water) were used in place of the ball, also that when hydrogen, carbon-dioxide or illuminating-gas were substituted for air, as a dielectric, the ball-and-point effect, more or less modified, could still be obtained. The investigation of these points, although it has already led to some results of significance, is as yet very incomplete.

Physical Laboratory of Cornell University,
September 1890.

XVI. *Conductivity of Hot Gases.*

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN, Cambridge, January 19, 1891.

IN the January number of Wiedemann's *Annalen* Dr. Arrhenius publishes an account of some experiments on the conductivity of hot vapours. His results differ from those obtained by me (Phil. Mag. April and May 1890) in the cases of the vapours of hydrochloric acid, hydriodic acid, and ammonium chloride. According to his experiments these vapours do not conduct appreciably better than air at the same temperature, while I found that their conductivities were very greatly in excess of that of air. The difference between these results is, I think, easily explained on the view given in my paper, that the conduction of electricity through hot gases is due to dissociation. The method employed by Dr. Arrhenius was to inject these substances into a flame; thus the hydrochloric-acid gas, for example, would be surrounded by a multitude of other gases, and especially by hydrogen. The presence of a large excess of hydrogen would retard the dissociation of a gas such as hydrochloric acid, of which hydrogen is one of the products of dissociation; for it is a well-recognized principle in the theory of dissociation, that it is retarded by the presence in excess of one of the products of dissociation. This has been verified by Wurtz, who found that an excess of PCl_3 stopped the dissociation of PCl_5. In Dr. Arrhenius's experiments the dissociation of the hydrochloric acid would thus be very much less than it was in mine, when the gas was heated by itself, and when the dissociation was large enough to be detected by chemical means. This, on the view that the conductivity is due to dissociation, would be sufficient to explain the difference in the results. I have found myself that the conductivity of HCl is very much reduced by dilution with hydrogen, more

so than when diluted with CO_2. The difference between the results for HI may be explained in the same way; and the case of ammonium chloride is practically the same as HCl, as it dissociates into NH_3 and HCl, and the NH_3 does not conduct.

I may say that it was the fear of the true conductivity of the hot gases being masked by secondary effects of this kind, combined with the high conductivity of the flame itself, which made me reject the use of flames in my experiments. In a flame the chemical conditions are so complex that it is almost impossible to obtain results whose interpretation is free from ambiguity.

Some other remarks of Dr. Arrhenius are due to a misinterpretation of my meaning. I never stated that if we had the same number of molecules per unit volume of HI and I, the HI would conduct better than the I. On the contrary, I regard the conductivity of both HCl and HI as due to some of the chlorine and iodine remaining dissociated after the molecules of the gas have been split up. Dr. Arrhenius also explains the small conductivity of a dissociated gas, such as iodine, when compared with the conductivity of an electrolyte, by asking, Who can tell how many of the atoms of the dissociated gas are uncharged? but if the atoms of the gas can be without charge why cannot those of a salt in solution? and if we admit the existence of uncharged, that is electrically inactive atoms, why should there be any connexion between electric conductivity and osmotic pressure?

I remain, Gentlemen,

Yours very truly,

J. J. Thomson.

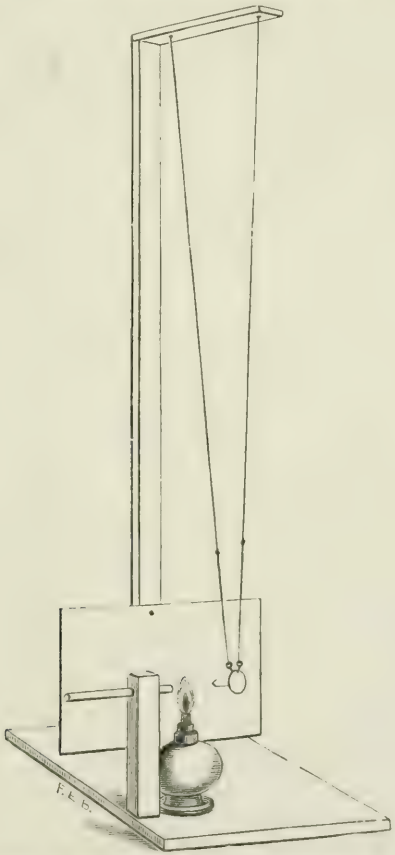
XVII. *A Lecture Experiment illustrating the Effect of Heat upon the Magnetic Susceptibility of Nickel.* *By* Shelford Bidwell, *M.A., F.R.S.**

IT is well known that iron when made red-hot loses its susceptibility and practically becomes a non-magnetic metal. Nickel becomes non-magnetizable at a much lower temperature, perhaps at about 300°. The following is a description of a simple piece of apparatus by means of which this effect may be shown as a lecture experiment.

A copper disk, to which a thin projecting tongue of nickel is soldered, hangs like the bob of a pendulum from a double thread. This bob is held on one side by a horizontally-fixed bar-magnet, which attracts and holds fast the nickel tongue when brought into contact with it. A spirit-lamp is placed

* Communicated by the Physical Society: read April 13, 1889.

beneath the tongue, and in a few seconds the heat of the flame temporarily destroys the magnetic quality of the nickel, so that the magnet can no longer hold it. The bob accordingly falls back and performs an oscillation. In the course of its excursion, however, the metal becomes cooler, and when it returns to the neighbourhood of the magnet the tongue is once more attracted. But after a momentary contact it is again liberated, and the process is repeated. If the position of the magnet and the size of the flame are properly adjusted, and care is taken to shield the apparatus from currents of air, the bob may be kept swinging for an indefinite period like the pendulum of a clock.



The apparatus is shown in the annexed figure, and its dimensions are as follows:—Diameter of the copper bob 5 centim., thickness 0·08 centim. Length of the projecting

portion of the nickel tongue 1·5 centim., width 0·8 centim., thickness 0·08 centim. The end of the nickel is filed to a blunt point (about 135°). A stout copper wire (0·14 centim. in diameter), to which the suspending thread is attached, passes through a hole drilled near the upper edge of the disk and is fixed by solder. The copper wire is bent in such a manner as to make the nickel tongue hang horizontally. The copper disk and the nickel tongue, except the extreme point of the latter, are coated with a mixture of lampblack and gold size to facilitate cooling by radiation. The length of the pendulum from the suspending beam to the centre of the bob is 85 centim. In order to prevent accidents by burning, the lower part of the suspension for a length of about 10 centim. is made of fine wire; the remainder consists of ordinary sewing-silk. The round bar-magnet is about 13 centim. long and 1·2 centim. in diameter; it slides stiffly through a horizontal hole in an upright post, and its best position must be found by trial. A sheet of white cardboard is fixed behind the bob, so that the effect may be well seen at a distance.

The above dimensions might no doubt be varied considerably without detriment; but if they are followed good results may be certainly obtained without waste of time in experiment.

XVIII. *Notices respecting New Books.*

An Elementary Treatise on Hydrodynamics and Sound. By A. B. Basset, *M.A., F.R.S., Trinity College, Cambridge.* Cambridge: Deighton, Bell, and Co. London: George Bell and Sons. 1890.

THIS is a "middle" treatise on the mathematical theory of Liquid-Dynamics, forming Part I., and Aero-Dynamics, to which Part II. is devoted, as far as needful for the elementary treatment of Sound. It is chiefly designed for students reading for Part I. of the Cambridge Tripos, or other Examinations, in which an elementary knowledge of its subjects is required; "but" the Author also trusts (to alter slightly his phraseology) "that it will not only be of service to those who have neither the time nor the inclination to become conversant with the intricacies of the higher mathematics, but will also prepare the way" for those intending to proceed to the higher parts of these subjects.

Some years back Lord Rayleigh, while filling the post of Cavendish Professor, threw out a suggestion that the instruction in Pure Mathematics of students who proposed to devote themselves mainly to Physics should be limited, as far as possible, to those parts which are indispensable to this object—a remark particularly applicable to the training of such a "middle" class of students as those for whom chiefly Mr. Basset writes, his present treatise requiring no more than "a knowledge of the elements of Differen-

tial and Integral Calculus and the fundamental parts of Dynamics." The endeavour has been "to solve the various problems which present themselves with the aid of the Principles of Energy or Momentum," fixed axes only being used in all but a few cases—which might be passed over by those whom the employment of moving axes would puzzle. Accordingly in Chap. I., on "Kinematic Theorems," in the few lines given to the Lagrangian Method the fact that the axes are considered fixed is emphasized; but there seems no reason why historical order should not be adhered to and the Eulerian given the priority to the Lagrangian method. Whatever room allows to be done in directing the student's attention to the history of the progress of his subject is valuable. So, later on, under "Dynamical Theorems"—as in the Author's excellent larger treatise—it is barely remarked that the principle involved in equation (30) is Bernoulli's Theorem; but to which of the gifted family it is due the student is left uninformed, as also of the work in which it was originally given—Bernoulli's *Hydrodynamica*, or John, his father's *Hydraulica*, 1738. In the case of living writers the references are more fully given. Dr. Glaisher, in his Address to Section A, British Association, Leeds Meeting of last year, made a valuable recommendation that in all Mathematical Treatises references should be given to the original memoirs &c. in which the results noticed first appeared. The late Mr. Gregory, following the precedent set by Dean Peacock, made such references (even if at second hand) a feature in his well-known 'Examples,' and Mr. Walton in his, on Dynamics and Hydrostatics, adhered to the precedent, thereby giving a rough skeleton-history of the subjects. It is, however, of more importance that condensation to save space should not be carried to the point of merely writing down a result without proof in cases where one of the classes of students for whom the treatise is intended could not fairly be considered competent—if willing to pause, in "getting up" the book, and make the effort—to supply the details of proof. This is the case when the equation [(7) Chap. I.] of continuity for liquids in Polar Coordinates is merely set down; while in the larger treatise the details of the proof are given, though not with the fulness which would be adequate to the wants of the reader of the present "Elementary" one. Besides those alluded to, subjects dealt with in this preliminary chapter are "Flow and Circulation," "Sources," and "Doublets" and the "Velocity-Potentials" due to them; "Images;" Rational Proofs of Torricelli's Theorem and of the least section of the Vena Contracta being a third harmonic to the areas of the (uniform) section of the vessel and that of the orifice, supposed horizontal, with no forces acting, but a uniform pressure on the upper surface. Connected with the last-mentioned subject there is an interesting and elementary discussion of the theory of the "Vena Contracta" for a gravitating liquid, the orifice being in the side of the vessel, by the late Mr. Hanlon; with a note thereon by Clerk-Maxwell in Lond. Math. Soc. Proc. vol. iii. pp. 4, 5.

Chapters II. and III. deal with some of the simpler cases of motion of solids in liquids. Chapter IV. is occupied with the important subjects of "Wave Motion," and "Stability of Fluid Motion." "Rectilinear Vortex Motion" forms the subject of Chapter V., ending the first part of the treatise, which occupies about five eighths of the whole book. The remaining chapters—VI., Introductory, on Sound; VII., on the "Vibrations of Strings and Membranes;" VIII., on the "Flexions of Bars; and IX., on the "Equations of Motion of a Perfect Gas,"—are mainly the more elementary portions of vol. i. of Lord Rayleigh's great treatise. With this might still advantageously be read (if yet procurable) Sir G. B. Airy's 'Lectures on Sound,' compiled for the use of students of the same mathematical status as those for whom Mr. Basset writes, at a time when their wants were wholly unprovided for. This manual, published in 1868, was the realization of a wish expressed to the author by the late Dean Peacock thirty years previous to its appearance. In fact at that time there was no separate treatise accessible to the English student but Sir J. F. W. Herschel's article (1830) on Sound, in the *Encyclopædia Metropolitana*.

To those acquainted with Mr. Basset's larger work it will be needless to dilate on the completeness with which he handles the subjects of the Elementary treatise as far as pursued—an article by Lord Rayleigh on Bells, as recent as January 1890, being drawn upon; and in clearness and vigour of style little remains to be desired. It might be suggested, perhaps, that the frequent use of the editorial "we," and its cases, would be advantageously replaced by other phrases, more in accordance with modern habit, in the second edition, to which the book is likely ere long to run. It was with a view to such an opportunity of revision and correction that the remarks in the earlier parts of this notice were directed. Otherwise it would have been more grateful to dwell on the numerous excellences of the work, which was perhaps rather hurried through the press to fill up, as soon as possible, the want it was the Author's object to meet.

J. J. W.

Notes on Trigonometry and Logarithms. By the Rev. J. M. Eustace, M.A. (London: Longmans, 1890.)

This is a work composed on the usual lines, the text of which is very correctly printed: there are of course slips here and there, but we need not specify them for our readers. The compiler's object has been to write a book for those students who have not the advantage of a "coach," and for such we consider he has made a capital selection, and we think he has treated his subject in a manner suitable for such readers. There is a large collection of examples taken from University and Civil Service Examination Papers. Two or three of the figures are incorrectly drawn. Answers to the Exercises accompany the work.

The Scientific Papers of James Clerk Maxwell. *Edited by* W. D. Niven, M.A., F.R.S. Two Vols., 4to : Cambridge, at the University Press.

At length this long-looked-for memorial work has appeared, in two substantial volumes, and will be welcomed by the many students of Maxwell, both in England and on the Continent, to whom the earlier papers were rather inaccessible.

There are some odd omissions; for instance, there is nothing about the determination of the B.A. standard of resistance. It may be regretted also, perhaps, that a few more of his less laborious contributions to science are not included in the collection, for all that he threw off was brilliant and suggestive, and one had hoped for something like a complete series of notes of his Lectures at Cambridge, but we must be thankful for such of the lighter productions as it has been decided to include. It is a great pity when in these collected works nothing but the solid memoirs are inserted. These of course must appear, but they are necessarily more or less known, and will naturally be hunted up by students of the particular branch; but the multifarious contributions to periodical literature of a great man are usually of far more than ephemeral interest, and though not of course ranking along with his serious productions, yet are very helpful and suggestive, and are extremely likely to get overlooked and forgotten.

A real memorial volume should, we think, include almost all that a man has thought it worth while to print, unless of obviously only temporary interest; but it is difficult to say what will not be interesting to posterity. Even a selection from correspondence might be judiciously included. How grateful we are now for mere scraps of private letters from Newton. Look at the little scrap thrown off to his friend Dr. Law, accidentally preserved, and printed in 'Nature,' May 12, 1881: to the eye of reverence and affection a personal glimpse like that is full of interest. It is hard for contemporaries to realize the view that posterity will take of the relative moment of the works of a man of genius. Sometimes a few brilliant flashes, now not quite intelligible, will, in the light of subsequently acquired knowledge, be even more highly appreciated than solid work that has become a semi-commonplace of science. It is for posterity that memorial volumes are largely intended, and from its point of view should they be regarded by its Editor.

A very interesting biographical preface by the Editor opens the first volume, which contains the boyish paper on Ovals, some Optics, the theory of Colour Perception, the paper on Lines of Force, and the great memoirs on Saturn's Rings and the Dynamical Theory of the Electromagnetic Field.

The second volume contains the papers on Viscosity and general Kinetic Theory of Gases, the determination of "v," the work on Graphical Statics, other matter more or less incorporated in the

'Electricity and Magnetism,' and a great number of articles, lectures, and reviews; the series of 'Encyc. Brit.' Physical articles, so far as life permitted them to be written by Maxwell's pen, being also inserted. It would have added to the interest if the dates had in all cases been affixed to the different memoirs, but they seem arranged in fairly chronological order.

The mere titles of the papers carry the mind over a large part of the field cultivated in recent years by what may be called "Section A," and the world must be grateful to the Clerk Maxwell Memorial Committee and the Syndics of the University Press for the liberal manner in which the work has been carried out.

O. J. Lodge.

XIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 66.]

December 17, 1890.—W. H. Hudleston, Esq., F.R.S., Vice-President, in the Chair.

THE following communications were read:—

1. "On Nepheline Rocks in Brazil—II. The Tingua Mass." By O. A. Derby, Esq., F.G.S.

In a former paper the general distribution of the nepheline rocks, so far as known, was given with a particular description of a single one, the Serra de Pocos de Caldas. The present paper treats of a second mass, the Serra de Tingua, a high peak of the Serra do Mar, some forty miles from Rio de Janeiro.

The peak is essentially a mass of foyaite rising to an elevation of 1600 metres, on the crest and close to the extremity of a narrow gneiss ridge of a very uniform elevation of about 800 metres. As seen from a distance, the conical outline and a crater-like valley on one side are very suggestive of volcanic topography. In the structure of the mass both massive and fragmental eruptives are found, the former greatly predominating.

The predominant rock is a coarse-grained foyaite which is found everywhere in loose blocks about the margins of the mass, but not extending beyond it. In the numerous cuttings in the immediate vicinity, dykes of phonolite and basic eruptives (augitite) are exceedingly abundant, foyaite never appearing in a dyke form. There is, however, abundant evidence that foyaite and phonolite are but different phases of the same magma.

Aside from the dyke phonolites, true effusive phonolites associated with fragmental eruptives (tuffa) were found high up in the crater-like valley, proving that the mass was a volcanic centre in the most restricted sense of the word.

This conclusion affords an explanation of some of the peculiarities of the foyaite, which has many characteristics of effusive eruptives

mingled with those of the deep-seated ones (*Tiefengesteine*). These have, aside from the porphyritic structure, a *schlieren* structure revealed by a peculiar fluted weathering (illustrated by a photograph) and the presence of pseudo-crystals in the form of leucite.

Stratigraphically the Tingua foyaites lie in sheet-like masses like lava-flows, extending from the higher to the lower portions of the mountain, the underlying gneiss being revealed at nearly all levels, wherever the mass has been scored by streams. The general fragmentary character of the rock seems to be due to the undermining of these sheets.

Specimens and photographs illustrating the peculiar pseudo-crystals in the form of leucite that occur in both the foyaites and phonolites of Tingua (although no leucite has been detected in the rock) were exhibited and discussed.

2. "The Variolitic Diabase of the Fichtelgebirge." By J. Walter Gregory, F.G.S., of the British Museum (Natural History).

The author has examined the variolitic diabases in the neighbourhood of Berneck, and adduces evidence of their having been intruded into the Devonian rocks before the latter were affected by the great earth-movements which have folded the palæozoic rocks of the district. He finds that the variolitic structure occurs in two different arrangements: (*a*) on the surfaces of spheroidal masses of compact diabase, which are comparable with those of Mt. Génèvre: (*b*) as a true contact-product on the selvage of the diabase, the latter being comparatively rare, and the varioles less perfectly developed.

He gives proofs that the varioles are true spherulites, and not fragments of Devonian rocks, as supposed by von Gümbel. He argues that though they are the product of rapid cooling, too sudden a solidification of the diabase may prevent their formation, and that for a similar reason the amygdaloidal is less variolitic than the compact diabase, the loss of the water that occupied the vesicles having diminished the fluidity of the rock. Finally, he maintains that the "pseudo-crystallites" are rifts and fissures due to contraction, and that the remarkable optical properties described by Michel-Lévy are due to the filling-up of cracks by felspathic matter deposited in optical continuity with the crystalline fibres on each side.

January 7, 1891.—Dr. A. Geikie, F.R.S., President, in the Chair.

The following communications were read:—

1. "On the North-west Region of Charnwood Forest, with other Notes." By the Rev. E. Hill, M.A., F.G.S., and Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S.

The paper contains the results of a re-examination of the North-west Region, when the authors had the advantage of using the six-inch Ordnance-map, published since the completion of their former work. In this they had expressed the opinion that the rock of Peldar Tor and that of High Sharpley were somewhat altered pyroclastics, being much influenced by the non-igneous origin asserted

for the "porphyroids" of the Ardennes. But in 1882 one of them had visited this region, and was then convinced that the porphyroids, which closely resembled the rock of Sharpley, were felstones which had been rendered schistose by subsequent pressure. The result of their subsequent work in Charnwood has convinced the authors that the rocks of Sharpley and of Peldar Tor are in the main of a like origin and history. The mass of Bardon Hill, where the quarries have been much enlarged, has also been studied, and some details in the section formerly published have been corrected. The schistose bands, on which the authors relied as marking horizons for stratigraphical purposes, prove to be zones of exceptional crush. The occurrence of a rock exactly resembling that of Peldar Tor is fully established. It is extremely difficult to decide upon the true nature of the rocks which are chiefly worked in the pit, but the authors remain of opinion that for most of them a pyroclastic origin is the more probable.

Some notes are added upon the relations of the holocrystalline igneous and the sedimentary rocks of the Forest, upon the Blackbrook group, and upon the fragments and pebbles in certain of the coarser ashy deposits. Some remarks are made upon the glacial phenomena exhibited in the Forest-region; these indicate that this cannot have been overridden by a great northern ice-sheet, and it does not afford the usual signs of the action of local glaciers. At the same time it has been a centre of dispersion for erratics, especially towards the south and south-west, these being found sometimes more than 20 miles away. Hence, in the opinion of the authors, the erratics have been distributed by floating ice during an epoch of general submergence. Some minor "corrigenda" in the earlier papers are noted, with certain changes in the names of localities, bringing them into harmony with the six-inch map.

2. "Note on a Contact-Structure in the Syenite of Bradgate Park." By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., V.P.G.S.

The author described a specimen, obtained at Bradgate Park, showing a junction of the syenite and slaty rock of Charnwood. The latter rock is very slightly altered; the former exhibits a number of grains of felspar and quartz set in a matrix which has now a "trachytic," now a devitrified structure. He traced the former into the "micrographic" structure observed generally in these syenites, and discussed its significance. His study of these structures in this and many other instances led him to infer that they generally indicated that the rock, at a late stage, had consisted of a mixture of previously formed crystalline grains and a viscous magma, that the temperature of the mass had been comparatively low, that it had cooled rather gradually, and that the condition of the magma—*i. e.* one of very imperfect fluidity—had not permitted of free molecular movements among its constituents. Thus this structure, together with certain others mentioned, might be regarded as indicative of "crystallization under constraint."

3. "On the Unconformities between the Rock-Systems underlying the Cambrian Quartzite in Shropshire." By Ch. Callaway, D.Sc., F.G.S.

I. *Review of the Evidence for the respective Ages of the Uriconian and Malvernian Rocks.*

The author criticises the conclusions arrived at by Prof. Blake (Q. J. G. S. 1890, p. 386), and adduces evidence to show:—

(1) That the felsites regarded by himself as Archæan have *not* been shown to be intrusive in Longmynd Rocks.

(2) That it has not been proved that the Longmynd Series is divisible into two groups, separated by an unconformity; and that, therefore, the evidence from included fragments remains unaffected.

(3) That the conglomerates and grits associated with the Uriconian are an integral part of that system, and are not of Cambrian age; and that the granitic and metamorphic land-masses from which so many of the fragments in the conglomerates are derived are consequently of pre-Uriconian age.

(4) That the granitic rocks of Shropshire are not intrusive in the Uriconian.

II. *The Relation between the Uriconian and the Longmyndian.*

Pending the publication of Prof. Lapworth's researches upon the fauna of the Hollybush Sandstone, the author regards it as hardly wise to assign positively a pre-Cambrian age to the Longmyndian system.

In favour of an actual break between the Uriconian and Longmyndian rocks, he gives details showing the general discordance of strike between the two groups; the locally concordant strikes are seen along a line of fault. Furthermore, as the junction between the two groups is faulted, this, whilst of course not proving an unconformity, renders incredible the hypothesis of conformity and igneous intrusion along the line of junction. Again, the conditions of deposit were different: the Uriconian is essentially a volcanic formation, whilst the Longmyndian rocks are characterized by their even sedimentation, and the author maintains that such a change of conditions must indicate a break in time, though the unconformity need not necessarily be very great.

Lastly, the occurrence of fragments of Malvernian granites and schists (formed at great depths) in the Uriconian Conglomerates indicates the existence of an unconformity between the holocrystalline and volcanic systems.

XX. *Intelligence and Miscellaneous Articles.*

CHANGES OF VOLUMES OF DIELECTRICS. BY D. BOS.

THE first of the three chapters into which the work is divided treats of the expansion observed by Duter, which hollow glass tubes and bulbs show when they are charged as Leyden jars.

The explanation of this phenomenon is sought for by Korteweg in the electrical pressure upon the sides of the flask. The author finds a sufficiently close agreement between the measurements made by Quincke and the calculations of Korteweg, if the magnitudes occurring in the formula—the dielectric constant, the difference of potential of the coatings, the coefficient of elasticity, and the thickness of the glass—are determined with sufficient accuracy.

The experiments of Julius and Korteweg with caoutchouc tubes, which show the influence of the coefficient of elasticity by a far greater expansion than glass tubes of the same thickness, are given as a strong reason for the opinion that the electrical pressure is the chief cause of the expansion.

A small part is ascribed to the heating of the dielectric.

In the second chapter the forces which occur during a charge of the dielectric are calculated. It is presupposed that with a relative contraction (g) of the dielectric in the direction of the lines of force, the dielectric constant k changes into $k(1+4\alpha g)$, and when the contraction is at right angles to the lines of force, into $k(1+4\beta g)$.

If F is the electromotive force at work in the dielectric, we get in the direction of the lines of force a tension $(k/8\pi+\alpha/2)F^2$ on the unit of surface, and at right angles to the lines of force a pressure $(k/8\pi-\beta/2)F^2$.

The author gives the developments of these expressions given by Helmholtz and by Lorberg, and compares the results with the experiments of Quincke on the attraction in the direction of the lines of force, the repulsion at right angles thereto, and the change of the dielectric constant with the magnitude of the electric forces.

It is laid down that the measurements have not yet attained such great accuracy as will permit of α and β being determined.

The third chapter discusses Quincke's observations of the expansions and contractions of dielectric liquids contained in a kind of voltameter whose plates are connected with the poles of a charged Leyden jar.

In agreement with Röntgen the author ascribes these changes of volume to a heating of the liquid, and the extremely small contraction of water at 0° to the very small negative coefficients of expansion, and to the great specific heat of water.

With an apparatus founded on Quincke's the author finds an expansion with rape oil, and also with almond oil, where Quincke found a contraction. By means of a thermometer it was further shown that on charging heat is produced between the plates which

follows the same course as the expansion, and is of the same order as is required by the expansion.

The changes of volume of gases are treated in conclusion, which Quincke could not observe, even with very accurate instruments, or only in one case with carbonic acid. The author doubts the validity of the calculation made by Lippmann (Mascart and Joubert's 'Electricity,' translated by Atkinson, vol. i. p. 632) on the basis of the principle of the conservation of electricity, which gives for carbonic acid 40 times as great a contraction as that found by Quincke, and also for other gases contractions which Quincke could not have overlooked.

From the same principle the author deduces that ideal gases could not show any change of volume.—*Inaugural Dissertation, Groningen*; *Beiblätter der Physik*, No. 11 (1890).

THE OPTICAL USEFUL EFFECT OF INCANDESCENT LAMPS.

BY E. BLATTNER.

The total energy imparted to an incandescent lamp, and in a stationary condition radiated by it, is $A_0 = i^2 r$. This energy consists of two parts, A_1 and A_2, which correspond to the radiation of heat and light respectively. If J is the mechanical equivalent of heat, and W_1 and W_2 the corresponding quantities of heat, $A_1 = JW_1$ and $A_2 = JW_2$. The optical useful effect is $A_2 A_0 = W_2 W_0$ and $W_0 = W_1 + W_2$. The author determined W_0 by placing the incandescent lamp in a thin copper cylinder blackened on the inside, which was filled with water and served as calorimeter, and which measured the rise of temperature. W_1 was measured by an exactly corresponding glass cylinder.

In order to measure i a special form of compass was used in front of the magnet; in the horizontal plane laid through the two poles of the magnet a wire rectangle was laid traversed by a current the sides of which run N.S. and E.W.; the former only act, and in opposite directions; by altering the distance from one another and from the magnet, the sensitiveness may be regulated.

If u is the angle of deflexion, a half the length of the sides of the rectangle, d_1 and d_2 the distance from the magnet, H the horizontal component of the earth's magnetism, the intensity of the current is

$$i = \frac{H}{C} \tan u, \quad C = \frac{2a^2 + d_1}{d_1(a^2 + d_1^2)} - \frac{2a^2 + d_2^2}{d_2(a^2 + d_2^2)}.$$

The difference of potential was measured partly by shunting and partly with the condenser, where it was compared with 10 Daniells. The intensities of the light were determined in standard candles with Bunsen's photometer. The following results were obtained:—

	A_0.	$\frac{A_2}{A_0}$	Brightness. K.
1. Swan lamp	4·895 10^8	0·023	2·62
	6·719 10^8	0·028	9·24
	7·523 10^8	0·036	13·24
	8·560 10^8	0·052	20·60
2. Edison lamp ...	5·818 10^8	0·036	4·01
	7·409 10^8	0·042	8·29
	9·259 10^8	0·062	16·98
	11·208 10^8	0·085	28·65
3. Bernstein lamp..	12·289 10^8	0·042	
	16·163 10^8	0·065	
	18·895 10^8	0·073	
	23·905 10^8	0·099	

The values deduced from the experiments show that incandescent lamps exhibit somewhat different deportment as regards conductivity. While the Swan lamp with a brightness of 20 candles gives an optical useful effect of 5 per cent., Edison and Bernstein lamps give for the same luminosity an effect of 7 per cent.

The optical useful effect of all the lamps increases with the temperature. With the highest temperature of incandescence, this can be raised to 10 per cent. With the normal temperature of ignition, when the luminosity is that near 16 candles, it does not exceed 5 to 6 per cent.; that is, of the total electrical energy used for working the incandescent lamp only 5 to 6 per cent. is available for illumination. The rest in the form of obscure radiation, amounting to 94–95 per cent., is lost as far as light is concerned.—*Inaugural Dissertation, Zürich*; *Beiblätter der Physik*, No. 11, 1890.

ON THE CONDUCTIVITY OF SNOW. BY S. A. HJELTSTRÖM.

From the great importance in nature of the thermal deportment of the snow layer, the author made experiments on the daily variations of the temperature at different depths in the snow, in order to calculate therefrom the thermal conductivity of snow. The bulbs of the thermometers were at a depth of 1, 11, 21, and 31 centim. below the surface of the snow. The snow near the thermometers was protected against the direct rays of the sun by a bank of snow on the south. The weather unfortunately did not allow of series of observations being carried on for a long time.

Taking the specific heat of snow as equal to that of ice, 0·50, and for its density the value determined on the spot by the author, 0·183, the absolute conducting-power may be determined from Ångström's formula to be

0·0269, 0·0343, 0·0302, Mean 0·0304,

the units being C.G.S. The conductivity of snow is accordingly about one seventh that of moist clay (0·226).—*Öfvers. Act. Stockholm*, xlvi. p. 669 (1889); *Beiblätter der Physik*, vol. xiv. p. 1196.

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XXI. *On the Illustration of the Properties of the Electric Field by Means of Tubes of Electrostatic Induction.* By J. J. Thomson, *M.A., F.R.S., Cavendish Professor of Experimental Physics, Cambridge* *.

I HAVE attempted in the following pages to develop a method of expressing the various processes which occur in the electric field in terms of changes in the form or position of tubes of electrostatic induction which are assumed to be distributed throughout the field, in the hope that it may help the student to obtain a physical interpretation of results which are perhaps too frequently regarded as entirely expressed by equations. Methods such as this, of materializing, as it were, mathematical conceptions, seem to have a use even where, as in the case of Electricity, the analytical theory is well established ; for any method which enables us to form a mental picture of what goes on in the electric field has a freshness and a power of rapidly giving the main features of a phenomenon, as distinct from the details, which few can hope to derive from purely analytical methods. Experience has, I think, shown that Maxwell's conception of electric displacement is of somewhat too general a character to lend itself easily to the formation of a conception of a mechanism which would illustrate by its working the processes going on in the electric field. For this purpose the conception of tubes of electrostatic induction introduced by Faraday seems to possess many advantages. If we regard these tubes as having a real physical existence, we may, as I shall endeavour

* Communicated by the Author.

to show, explain the various electrical processes,—such as the passage of electricity through metals, liquids, or gases, the production of a current, magnetic force, the induction of currents, and so on,—as arising from the contraction or elongation of such tubes and their motion through the electric field.

We might, as we shall see, have taken the tubes of magnetic force as the quantity by which to express all the changes in the electric field; the reason I have chosen the tubes of electrostatic induction is that the intimate relation between electrical charges and atomic structure seems to point to the conclusion that it is the tubes of electrostatic induction which are most directly involved in the many cases in which electrical charges are accompanied by chemical ones.

We may regard the method from one point of view as being a kind of molecular theory of electricity, the properties of the electric field being explained as the effects produced by the motion of multitudes of tubes of electrostatic induction; just as in the molecular theory of gases the properties of the gas are explained as the result of the motion of its molecules.

As the principal reason for expressing the effects in terms of the tubes of electrostatic induction is the close connexion between electrical and chemical properties, we shall begin by considering at some length the connexion between these tubes of electrostatic induction and the atoms of bodies.

We assume, then, that the electric field is full of tubes of electrostatic induction, that these are all of the same strength, and that this strength is such that when a tube falls on a conductor it corresponds to a negative charge on the conductor equal in amount to the charge which in electrolysis we find associated with an atom of a univalent element.

These tubes must either form closed circuits or they must end on atoms, any unclosed tube being a tube connecting two atoms. In this respect the tubes resemble lines of vorticity in hydrodynamics, as these lines must either be closed, or have their extremities on a boundary of the fluid.

We may suppose that associated with these tubes of electrostatic induction there is a distribution of velocity, both in themselves and in the surrounding æther, and that the energy due to this motion of the medium constitutes the energy which is distributed throughout the electric field. In addition to there being this energy in the medium, the incidence of a tube of force on an atom may modify the internal motion of the atom, and thus alter its energy, so that, in addition to the energy in the field, there may be a certain amount of

energy due to the alteration in the motion of the atoms: this may be represented by the addition to the ordinary expression for the energy of a term w for each atom on which a unit tube falls, $-w$ for each atom which a tube leaves; we shall suppose that w depends on the nature of the atom, that it is not the same for zinc as for copper and so on. The existence of this energy will produce the same effect as if the atoms of different substances attracted electricity with different degrees of intensity: this is the assumption made by von Helmholtz, and it has been shown by him to be sufficient to account for contact electricity.

The ends of an unclosed tube of induction are places where electrification exists, and therefore are always situated on matter. According to our view, the ends of a tube of finite length are on free atoms as distinct from molecules, the atoms in the molecule being connected by a short tube whose length is of the order of the molecular distance. On this view, therefore, the existence of free electricity, whether on a metal, an electrolyte, or a gas, always denotes the existence of free atoms. The production of electrification must be accompanied by chemical dissociation, the disappearance of it by chemical combination; changes in electrification are on this view always accompanied by chemical changes. This was long thought to be a peculiarity of the passage of electricity through electrolytes, but recent experiments seem to show that it is also the case when electricity passes through gases. Thus, for example, those gases which conduct readily when hot are those which dissociate when heated, and are thus undergoing chemical changes when the electricity passes through them. Again, it is known that the passage of electricity through many gases causes chemical changes to take place—the production of ozone is the most familiar instance of this, but there are a multitude of others. Lastly, R. v. Helmholtz and Richarz have found that when electricity passes through a gas, a steam-jet in the neighbourhood is influenced in the same way as it is when free atoms are produced by chemical changes. All these results seem to point to the conclusion that the passage of electricity through gases is accompanied by changes in the pairing of the atoms of the gas. Although we have no such direct evidence of the same effect when electricity passes through metals, it must be borne in mind that direct evidence in this case is very much more difficult to obtain, and there are many reasons for taking the view that the passage of electricity through metals is performed in much the same way as it is through electrolytes and gases.

We will begin by considering how metallic conduction differs from electrolytic. In the first place, as the temperature increases the conductivity of electrolytes, as a general rule, increases, while that of metals diminishes. This rule is not, however, without exceptions: there are cases in which, though the conduction is not usually supposed to be electrolytic, the conductivity increases as the temperature increases. Carbon is a striking instance of this, and quite lately Feussner has prepared alloys of manganese and copper whose conductivities show the same peculiarity. These exceptions are sufficient to show that increase of conductivity with the temperature is not a sufficient test to separate electrolytic from metallic conduction.

If we regard the passage of electricity through a body as essentially bound up with chemical changes, it does not seem surprising that an increase in temperature may produce opposite effects on the conductivities of two substances, even though in both cases the conduction was effected by changes in the pairings of the atoms. For the action of an increase of temperature has a two-fold effect on the processes which, on this view, accompany electric conduction. In the first place, it may promote the splitting up of the molecules into atoms which, on this theory, forms one part of the process of conduction; but, on the other hand, after the molecules are split up it retards their reunion, which forms another part of the process. And, again, an increase in the temperature increases the distance between the molecules, and this will also retard the rate at which chemical interchange takes place. The fact that the metals are solids is no reason why the conductivity through them should not be electrolytic in its nature, for there are many instances of solid electrolytes: thus Lehmann has shown that electrolysis takes place through a crystal of silver iodide placed between silver electrodes without any change being perceptible in the shape or size of the crystal, though it was watched through a microscope whilst the current was passing.

With regard to the appearance of the products of chemical decomposition at the electrodes, we could not expect to get any evidence of this in the case of the elementary metals: the case of alloys seems more hopeful; but Professor Roberts Austen has examined several alloys through which a powerful current had been passed without detecting any difference in the composition of the alloy at the terminals. This result does not, however, seem to me to prove that the conduction was not electrolytic; for some alloys are little more than mixtures, whilst others behave as if they were solutions of one

metal in another; and in neither of these cases could we expect to get any change in the composition of the alloy at the electrodes. We could only expect to find this when we used an alloy in which the connexion between the constituents could be regarded as of such a definite character that in the molecule of the alloy one metal could be regarded as the positive, the other as the negative element. The alloys used by Prof. Roberts Austen do not seem to have been of this character. The reasons which account for the absence of change in the constitution of the alloy at the electrodes will also account for the absence of polarization.

Though the electrical conductivities of the metals are enormously greater than those of electrolytes, there does not seem to be any abrupt change from the conductivity in cases where it is manifestly electrolytic, such as fused lead chloride, to those in which it is not recognized as being of that nature, as in carbon. The following table, giving the electric conductivity of some substances, will show this :—

Silver	63
Mercury	1
Gas-carbon	1×10^{-3}
Tellurium	4×10^{-4}
Fused lead chloride	2×10^{-4}

There is a greater disproportion between the thermal conductivities of silver and cement than there is between the electrical conductivities of mercury and fused lead chloride; but no one argues that, on this account, the method by which heat is propagated in silver is essentially different from that by which it is propagated in cement.

It is also suggestive that the substances which are intermediate in their chemical properties between the metals and the non-metals, such as phosphorus, selenium, and tellurium, possess properties with regard to metallic conduction intermediate between those of metals and electrolytes,—thus, as shown by W. Siemens, the resistance of some of the modifications of selenium increases with the temperature, while that of other modifications diminishes,—and that some of the modifications seem to show polar effects,—thus, when one electrode is large and the other small, the current is greater when the large electrode is negative than when it is positive. The changes in the chemical properties of the substance seem to proceed step by step with the changes in their behaviour with regard to electrical conduction.

If we accept the electromagnetic theory of light, we have

an additional reason for supposing that the processes concerned in metallic conduction are the same as those in electrolytic. For the opacity of thin metal films is enormously less than that theory would indicate, if the conductivity of the film for the very rapid electrical vibrations which constitute light were the same as for steady currents. In this respect the metals behave very much like electrolytes, for these act as dielectrics to the light vibrations and as conductors for steady or oscillating currents, provided the period of vibration is very much greater than that of the light-vibrations. On the view we have taken of metallic conduction, since the process of dissociation and recombination takes a finite time, if the polarization is reversed in less than this time, the old polarization will not have had time to disappear before the new is superposed, and the metal will, under these circumstances, behave more like an insulator than a conductor.

We can easily find an expression for the time T taken by a tube of electrostatic induction to disappear (that is, to contract to a length comparable with that between the atoms of a molecule). Let E be the electromotive intensity at any point, K the specific inductive capacity of the medium ; then the number of tubes of electrostatic induction passing through unit area is

$$\frac{K}{4\pi} E.$$

Since T is the time taken by one tube to disappear, the number of tubes which disappear in the conductor in unit time is $KE/4\pi T$; the number of tubes which disappear in unit time is equal, however, to the current c through unit area. Hence

$$c = \frac{KE}{4\pi T}.$$

Thus $4\pi T/K$ is the specific resistance σ of the conductor ; hence, if $\{K\}$ be the electrostatic measure of K, we have

$$T = \frac{K}{4\pi} \frac{\sigma}{9 \times 10^{20}}.$$

The following table contains the values of T/K for a few substances :—

Silver	$1{\cdot}5 \times 10^{-19}$
Lead	$1{\cdot}8 \times 10^{-18}$
Water with 8·3 per cent. of H_2SO_4 .	$3{\cdot}1 \times 10^{-13}$

The value of K for anything like a good conductor has never been measured ; but since substances which show the

least trace of conductivity, such as water or alcohol, have specific inductive capacities ranging from 70 to 100, it is probable that for good conductors K is exceedingly large. If, however, its value for metals were no greater than that for distilled water, the time required for the disappearance of a tube of force would be comparable with the time of vibration of a light-wave; so that the conductivity would be much smaller for these waves than for steady currents.

We may picture to ourselves the tubes of electrostatic induction shortening in a conductor in some such way as the following:—Let us take the case of a condenser discharging through the gas separating its plates. Then, before discharge, we have a tube stretching from an atom O on the positive plate to another atom P on the negative one. The molecules AB, CD, . . . of the intervening gas will be polarized by the induction, the tubes of force connecting the atoms in these molecules pointing in the negative direction; as the strength of the field increases the tube in the molecule AB will lengthen and bend towards the tube OP, until when the field is sufficiently strong the molecular tube runs up into the tube OP. The tubes then break up into two tubes OA and PB, and the tube OA shortens to molecular dimensions. The result of this operation is that the tube PO has shortened to PB, and the atoms O and A have formed a molecule. This process is then continued from molecule to molecule until the tube PO has contracted to molecular dimensions. Instead of the tube PO jumping from molecule to molecule, several molecules may form a chain and be affected at once; in this case the tube would shorten by the length of the chain in the same time as on the previous hypothesis it shortened by the distance between two molecules.

The remarkable agreement between the values of the velocity of the ions as calculated by Hittorf and Kohlrausch and those found by Prof. Lodge in the experiments described in the British Association Report, 1887, makes it essential that any theory of conduction through electrolytes should lead to the same expressions for the ionic velocities. According to the preceding theory of conduction, if the molecules of the electrolyte form chains between the electrodes, the sum of the distances traversed by the anion and cation each time the tube of electrostatic induction breaks down is d, where d is the distance between two molecules of the electrolyte measured along a tube of induction. If the tube breaks down n times a second, the sum of the distances traversed by the ion and cation in one second is nd; so that, if u and v are the velocities of the anion and cation respectively, $u+v=nd$.

If ϵ is the charge on one of the atoms of the electrolyte, m the number of molecules per unit of area of a plane in the electrolyte parallel to the electrodes, then, when the molecules are polarized, the charge per unit area on the end of the chain of molecules is $m\epsilon$; this equals the surface-density on the electrodes $\mathrm{KE}/4\pi$, where E is the electromotive intensity and K the specific inductive capacity of the electrolyte. Hence

$$m\epsilon = \frac{\mathrm{K}}{4\pi}\mathrm{E}.$$

If c be the conductivity of the electrolyte, N the number of molecules in unit volume, we have

$$\frac{\mathrm{K}}{4\pi}n = c, \quad m = \mathrm{N}d.$$

Making these substitutions, we find

$$u+v = \frac{c\mathrm{E}}{\mathrm{N}\epsilon},$$

which is the same as the expression for the sum of the velocities given by Kohlrausch. The ratio of the velocities will follow exactly the same way from the migration-data whichever theory we adopt; so that there is nothing in Prof. Lodge's confirmation of Kohlrausch's expressions for the velocity of the ions inconsistent with the theory of conduction we are describing.

We will now leave the consideration of the behaviour of these tubes in conductors, and proceed to discuss their properties when moving through the dielectric.

Let f, g, h denote the number of unit tubes parallel to the axes of x, y, z respectively—in other words, the components of the electric displacement; and let us suppose that these tubes are moving with the velocity u, v, w parallel to the axes of coordinates.

Let us consider the increase in the number of tubes parallel to x which occurs in a time δt in an element of volume dx, dy, dz.

The increase due to the passage of the tubes across the faces of the element is

$$-\delta t\left(\frac{d}{dx}(fu)+\frac{d}{dy}(fv)+\frac{d}{dz}(fw)\right)dx\,dy\,dz.$$

The increase due to the deformation of the tubes inside the element is

$$\delta t\left(f\frac{du}{dx}+g\frac{du}{dy}+h\frac{du}{dz}\right)dx\,dy\,dz.$$

The rate of increase in the number of tubes parallel to x is thus

$$f\frac{du}{dx}+g\frac{du}{dy}+h\frac{du}{dz}-\left(\frac{d}{dx}(fu)+\frac{d}{dy}(fv)+\frac{d}{dz}(fw)\right);$$

which may be written as

$$\frac{d}{dy}(gu-fv)-\frac{d}{dz}(fw-hu)-u\left(\frac{df}{dx}+\frac{dg}{dy}+\frac{dh}{dz}\right);$$

and

$$\frac{df}{dx}+\frac{dg}{dy}+\frac{dh}{dz}=\rho,$$

ρ being the density of the free electricity.

Hence df/dt, the rate of increase in the number of tubes parallel to x, may be written as

$$\frac{df}{dt}=\frac{d}{dy}(gu-fv)-\frac{d}{dz}(wf-uh)-u\rho;$$

and similarly

$$\frac{dg}{dt}=\frac{d}{dz}(vh-wg)-\frac{d}{dx}(gu-fv)-v\rho,$$

$$\frac{dh}{dt}=\frac{d}{dx}(wf-uh)-\frac{d}{dy}(vh-wg)-w\rho.$$

But since $\frac{df}{dt}+u\rho$, $\frac{dg}{dt}+v\rho$, $\frac{dh}{dt}+w\rho$ are the components of the current parallel to x, y, z, we have, if α, β, γ are the components of the magnetic force,

$$4\pi\left(\frac{df}{dt}+u\rho\right)=\frac{d\gamma}{dy}-\frac{d\beta}{dz},$$

$$4\pi\left(\frac{dg}{dt}+v\rho\right)=\frac{d\alpha}{dz}-\frac{d\gamma}{dx},$$

$$4\pi\left(\frac{dh}{dt}+w\rho\right)=\frac{d\beta}{dx}-\frac{d\alpha}{dy}.$$

Hence we may regard the moving tubes of electrostatic induction as producing a magnetic force whose components α, β, γ parallel to the axes of x, y, z are given by

$$\left.\begin{aligned}\alpha&=4\pi(hv-gw),\\ \beta&=4\pi(fw-hu),\\ \gamma&=4\pi(gu-fv).\end{aligned}\right\}\quad\ldots\ldots\quad(1)$$

In other words, a moving tube of electrostatic induction may be regarded as producing a magnetic force at right

angles both to itself and the direction in which it is moving, and whose magnitude is 4π times the strength of the tube multiplied by its velocity at right angles to its direction. The direction of the force is such that the magnetic force and rotation from the direction of motion to that of the tube are related like translation and rotation in a right-angled screw.

Let us first consider the case where all the tubes are moving with the same velocity in a field whose magnetic permeability is unity.

The energy in the magnetic field per unit volume is

$$\frac{1}{8\pi}(\alpha^2+\beta^2+\gamma^2),$$

or substituting for α, β, γ their values from (1),

$$2\pi\{(hv-gw)^2+(fw-hu)^2+(gu-fv)^2\}.$$

The momentum U per unit volume parallel to x is the differential coefficient of this expression with respect to u, *i.e.*

$$4\pi\{g(gu-fv)-h(fw-hu)\},$$

or

$$\mathrm{U}=g\gamma-h\beta.$$

Similarly, if V, W are the components of the momentum parallel to y and z, we have

$$\left.\begin{aligned}\mathrm{V}&=h\alpha-f\gamma,\\ \mathrm{W}&=f\beta-g\alpha.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Thus the momentum per unit volume possessed by the moving tube is at right angles to the tube and to the magnetic force produced by it, and equals the product of the strength of the tube and the magnetic force.

The electromotive intensity parallel to x produced by the moving tube can be got by differentiating the expression for the Kinetic Energy with respect to f; in this way we obtain the following expressions for X, Y, Z, the components of the electromotive intensity:—

$$\left.\begin{aligned}\mathrm{X}&=w\beta-v\gamma,\\ \mathrm{Y}&=u\gamma-w\alpha,\\ \mathrm{Z}&=v\alpha-u\beta.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus the electromotive intensity produced by the motion of the tube is equal to the product of the velocity of the tube and the magnetic force produced by it, and is at right angles to

both the direction of motion of the tube and the magnetic force produced by it.

From equation (3) we see that

$$\frac{dZ}{dy}-\frac{dY}{dz}=v\frac{d\alpha}{dy}+w\frac{d\alpha}{dz}-u\left(\frac{d\beta}{dy}+\frac{d\gamma}{dz}\right)+\alpha\left(\frac{dv}{dy}+\frac{dw}{dz}\right)-\beta\frac{du}{dy}-\gamma\frac{du}{dz};$$

or, since

$$\frac{d\alpha}{dx}+\frac{d\beta}{dy}+\frac{d\gamma}{dz}=0,$$

we have

$$\frac{dZ}{dy}-\frac{dY}{dz}=\frac{d}{dx}(u\alpha)+\frac{d}{dy}(v\alpha)+\frac{d}{dz}(w\alpha)-\alpha\frac{du}{dx}-\beta\frac{du}{dy}-\gamma\frac{du}{dz}. \quad (4)$$

The right-hand side of this equation is equal to $-\frac{d\alpha}{dt}$, the rate of diminution in the number of tubes of magnetic force parallel to the axis of x.

Hence, since

$$\int(Xdx+Ydy+Zdz)$$

taken round a closed circuit is equal to

$$\iint\left\{l\left(\frac{dZ}{dy}-\frac{dY}{dz}\right)+m\left(\frac{dX}{dz}-\frac{dZ}{dx}\right)+n\left(\frac{dY}{dx}-\frac{dX}{dy}\right)\right\}dS,$$

taken over any surface entirely surrounded by the circuit, if l, m, n are the direction-cosines of the normal to the surface, we see by (4) that the line-integral of the electromotive force taken round a closed circuit is equal to the rate of diminution of the number of lines of magnetic force passing through the circuit.

Collecting these results, we see that a tube of electrostatic induction when in motion produces (1) a magnetic force at right angles to the tube and the direction of motion, (2) a momentum at right angles to the tube and the magnetic force produced by it, (3) an electromotive intensity at right angles to the direction of motion of the tube and the magnetic force produced by it.

The momentum and the electromotive intensity are thus both in the plane containing the direction of the tube and its velocity; the first of these is at right angles to the tube, the second to the velocity.

We have hitherto only considered the case of one tube, or rather of a set of tubes, moving with a common velocity. We can, however, without difficulty extend these results to the

case where we have any number of tubes moving with any velocities.

Let us suppose we have the tubes f_1, g_1, h_1 moving with the velocities u_1, v_1, w_1, the tubes f_2, g_2, h_2 moving with the velocities u_2, v_2, w_2, and so on. Then the rate of increase in the number of tubes in the element is

$$\Sigma\left(f\frac{du}{dx}+g\frac{du}{dy}+h\frac{du}{dz}\right)-\Sigma\left(\frac{d}{dx}(fu)+\frac{d}{dy}(fv)+\frac{d}{dz}(fw)\right).$$

This may be written as

$$\frac{d}{dy}\Sigma(gu-fv)-\frac{d}{dz}\Sigma(fw-hu)-\Sigma u\rho.$$

Hence we see, as before, that the collection of tubes may be regarded as producing a magnetic force whose components α, β, γ are given by

$$\left.\begin{aligned}\alpha &= 4\pi\Sigma(hv-gw),\\ \beta &= 4\pi\Sigma(fw-hu),\\ \gamma &= 4\pi\Sigma(gu-fv).\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The kinetic energy T per unit volume due to the motion of these tubes is

$$\frac{1}{8\pi}(\alpha^2+\beta^2+\gamma^2)$$

or

$$2\pi\left[\{\Sigma(hv-gw)\}^2+\{\Sigma(fw-hu)\}^2+\{\Sigma(gu-fv)\}^2\right].$$

Thus the momentum parallel to x of the tube with suffix (1) $d\mathrm{T}/du_1$

$$\begin{aligned}&= 4\pi\{g_1\Sigma(gu-fv)-h_1\Sigma(fw-hu)\}\\ &= g_1\gamma-h_1\beta.\end{aligned}$$

Thus the components U, V, W of the momenta parallel to the axes of x, y, z respectively are given by the equations

$$\left.\begin{aligned}\mathrm{U} &= \gamma\Sigma g-\beta\Sigma h,\\ \mathrm{V} &= \alpha\Sigma h-\gamma\Sigma f,\\ \mathrm{W} &= \beta\Sigma f-\alpha\Sigma g.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus, when we have a number of tubes moving about, the resultant momentum at any point is perpendicular to both the resultant magnetic force and the resultant electric displacement, and is equal to the product of these two quantities into the sine of the angle between them.

The electromotive intensity X parallel to the axis of x is equal to the mean of $d\mathrm{T}/df$.

Hence

$$\left.\begin{aligned} \mathrm{X} &= 4\pi\left(\overline{w\Sigma(fw-hu)} - \overline{v\Sigma(gu-fv)}\right) \\ &= \left(\overline{w\beta} - \overline{v\gamma}\right) \\ &= \beta\bar{w} - \gamma\bar{v}. \end{aligned}\right\} \quad . \quad . \quad (7)$$

Similarly, if Y and Z are the components parallel to the axes of y and z, we have

$$\mathrm{Y} = \gamma\bar{u} - \alpha\bar{w},$$
$$\mathrm{Z} = \alpha\bar{v} - \beta\bar{u},$$

where a bar placed over any quantity indicates that the mean value of the quantity is to be taken.

Thus, when a system of tubes of electrostatic induction is in motion, the electromotive intensity is at right angles both to the resultant magnetic force and the mean velocity, and is equal to the product of these two quantities into the sine of the angle between them.

From the preceding equations, we see that if we have a great number of positive and negative tubes moving about, if the positive tubes move in one direction and the negative ones in the opposite, there will be a resultant magnetic force, but if there are as many positive as negative tubes in each unit of volume, there will be no resultant momentum ; and if there are as many moving in one direction as the opposite, there will be no resultant electromotive intensity, due to the motion of these tubes. We see then that when the electromagnetic field is in a steady state, the motion of the tubes of electrostatic induction in the field will be a kind of shearing of the positive past the negative tubes, the positive tubes moving at one direction, and the negative at an equal rate in the opposite. When, however, the field is not in a steady state, this ceases to be the case, and then the electromotive forces due to induction are developed.

We get from equation (7),

$$\frac{d\mathrm{Z}}{dy} - \frac{d\mathrm{Y}}{dz} = \frac{d}{dx}(u\alpha) + \frac{d}{dy}(v\alpha) + \frac{d}{dz}(w\alpha) - \left(\alpha\frac{d\bar{u}}{dx} + \beta\frac{d\bar{u}}{dy} + \gamma\frac{d\bar{u}}{dz}\right),$$

since

$$\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz} = 0.$$

If we suppose the magnetic lines of force to be moving with the velocities $\bar{u}$, $\bar{v}$, $\bar{w}$, the right-hand side of this equation represents the rate of diminution of α.

When the tubes of electrostatic induction enter a conductor, their ends, as we have seen, get attached to atoms of the conductor, and the momentum of the tube gets transferred to the conductor. Let us consider a small portion of a conductor conveying a current, the area of the portion being so small that we may consider the magnetic force over it to be constant. The momentum parallel to x of a tube entering it is

$$g\gamma - h\beta ;$$

thus the momentum parallel to x which enters the element in unit time is

$$\iint \Sigma \{(g\gamma - h\beta)(lu + mv + nw) dS,$$

where dS is an element of the surface of the element, and l, m, n the direction-cosines of the normal to this surface. The above expression may be written in the form

$$\gamma \iint \Sigma \{ g\ (lu + mv + nw)\}\ dS - \beta \iint \Sigma \{h(lu + mv + nw)\} dS.$$

Now

$$\iint \Sigma \{g(lu + mv + nw) dS,$$

and

$$\iint \Sigma \{h(lu + mv + nw) dS$$

are the number of tubes of force parallel to x and y respectively which enter the element in unit time, that is, they are the components q and r of the current parallel to y and z respectively. Thus the momentum parallel to x communicated in unit time to the conductor, in other words, the force parallel to x acting on the conductor, is equal to

$$\gamma q - \beta r.$$

Similarly, the forces parallel to y and z are respectively

$$\alpha r - \gamma p,$$
$$\beta p - \alpha q.$$

These are the ordinary expressions for the force acting on a conductor carrying a current in a magnetic field.

When, as in the above investigation, we regard the force on a conductor carrying a current as due to the tubes of electrostatic induction which enter the circuit giving up their momentum to it, the origin of the force between two currents will be very much the same as that of the attraction between two bodies on Le Sage's theory of gravitation. Thus, for example, let us take the case of two straight parallel currents, A and B, flowing in the same direction, and let us suppose that A is to the left of B ; then more tubes of force will enter A from

the left than from the right, because some of those which would have come from the right if B had been absent will be absorbed by B; thus in unit time more momentum having the direction of left to right will enter A than that having the opposite direction ; thus A will move towards the right, that is, towards B, while for a similar reason B will move towards A.

We have now shown that we can explain the properties of the electromagnetic field if we suppose that throughout that field tubes of electrostatic induction in rapid motion are distributed, and that we can obtain the ordinary equations of the electromagnetic field if we start with the principle that the line-integral of the magnetic force round a closed curve is equal to the rate of increase of the number of tubes of electrostatic induction passing through that curve.

We shall now proceed to discuss some special problems by the light of this theory. The first we shall take is that of a sphere charged with electricity, and moving with the velocity w parallel to the axis of z. When things have reached a steady state, we may suppose that the sphere and the tubes of electrostatic induction emanating from it move like a solid body: we shall now consider the effect produced by pushing these tubes of force through the æther. Thus, if α, β, γ are the components of the magnetic force at any point, f, g, h those of the electric displacement at the same point, we have, by equation (1),

$$\alpha = -4\pi w g,$$
$$\beta = 4\pi w f,$$
$$\gamma = 0.$$

If X_1, Y_1, Z_1 are the components of the electromotive intensities due to the motion of the tubes of electrostatic induction, we have, by equation (3),

$$X_1 = w\beta,$$
$$Y_1 = -w\alpha,$$
$$Z_1 = 0.$$

The total electromotive intensity, whose components are X, Y, Z, will be given by the equations

$$X = \quad w\beta - \frac{d\psi}{dx},$$
$$Y = -w\alpha - \frac{d\psi}{dy},$$
$$Z = \quad -\frac{d\psi}{dz};$$

where ψ is a function which we must proceed to determine.

Substituting the above values for α and β, and remembering that

$$X=\frac{4\pi}{K}f, \quad Y=\frac{4\pi}{K}g, \quad Z=\frac{4\pi}{K}h,$$

we get

$$\frac{4\pi}{K}f=4\pi w^2 f-\frac{d\psi}{dx},$$

$$\frac{4\pi}{K}g=4\pi w^2 g-\frac{d\psi}{dy},$$

$$\frac{4\pi}{K}h= \quad -\frac{d\psi}{dz}.$$

Putting $1/K=V^2$, where V is the velocity of light through the dielectric, and remembering that

$$\frac{df}{dx}+\frac{dg}{dy}+\frac{dh}{dz}=0.$$

we get

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\left(1-\frac{w^2}{V^2}\right)\frac{d^2\psi}{dz^2}=0,$$

which, if

$$z_1=\frac{z}{\left\{1-\frac{w^2}{V^2}\right\}^{\frac{1}{2}}},$$

may be written as

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz_1^2}=0.$$

The solution of which is

$$\psi=\frac{A}{\{x^2+y^2+z_1^2\}^{\frac{1}{2}}}.$$

Since

$$(V^2-w^2)f=-\frac{1}{4\pi}\frac{d\psi}{dx},$$

$$(V^2-w^2)g=-\frac{1}{4\pi}\frac{d\psi}{dy},$$

$$V^2h=-\frac{1}{4\pi}\frac{d\psi}{dz}.$$

And since

$$\iint\left(f\frac{x}{a}+g\frac{y}{a}+h\frac{z}{a}\right)dS=e,$$

when the integration is extended over a sphere of radius a concentric with the moving sphere, and e is the charge on

that sphere, substituting the values of f, g, h in this equation in terms of ψ we find, if $w/V < 1$,

$$A = eV\sqrt{V^2 - w^2}.$$

Thus the electrostatic potential ϕ is given by the equation

$$\psi = \frac{e\left\{1-\frac{w^2}{V^2}\right\}^{\frac{1}{2}}V^2}{\left(x^2+y^2+\frac{z^2}{1-\frac{w^2}{V^2}}\right)^{\frac{1}{2}}}.$$

Thus the tubes of induction are no longer uniformly distributed, but are, in consequence of the electrical inertia, crowded towards the region in proximity to the equatorial plane of the sphere, where the displacements do not vary so quickly as along the axis.

The displacements are radial and are given by

$$\frac{f}{x}=\frac{g}{y}=\frac{h}{z}=\frac{e}{4\pi\left\{1-\frac{w^2}{V^2}\right\}^{\frac{1}{2}}}\frac{1}{\left(x^2+y^2+\frac{z^2}{1-\frac{w^2}{V^2}}\right)^{\frac{3}{2}}}.$$

The components α and β of the magnetic force are given by

$$\alpha = -\frac{ewy}{\left\{1-\frac{w^2}{V^2}\right\}}\frac{1}{\left(x^2+y^2+\frac{z^2}{1-\frac{w^2}{V^2}}\right)^{\frac{3}{2}}},$$

$$\beta = \frac{ewx}{\left(1-\frac{w^2}{V^2}\right)^{\frac{1}{2}}}\frac{1}{\left(x^2+y^2+\frac{z^2}{1-\frac{w^2}{V^2}}\right)^{\frac{3}{2}}}.$$

(See Heaviside, Phil. Mag. April 1889 ; J. J. Thomson, Phil. Mag. July 1889.)

The momentum in the medium is at right angles to the displacement and the magnetic force, and is therefore at right angles to the radius in the plane containing the radius and the direction of motion ; its magnitude per unit volume is by equation (2),

$$\frac{w}{4\pi}\frac{e^2}{1-\frac{w^2}{V^2}}\cdot\frac{x^2+y^2}{\left(x^2+y^2+\frac{z^2}{1-\frac{w^2}{V^2}}\right)^3}$$

Let us now suppose that the sphere is moving in a uniform

field of magnetic force, where the components of the external magnetic force are $\alpha_0, \beta_0, \gamma_0$, the momentum per unit volume parallel to x is

$$g\gamma_0 - h(\beta_0 + 4\pi wf) ;$$

the rate at which this momentum enters a sphere concentric with the moving sphere is

$$\iint \frac{1}{r} \{g\gamma_0 - h(\beta_0 + 4\pi wf)\} zw dS,$$

where dS is an element of the surface of the sphere whose radius is r. Integrating this we get

$$-e\beta_0 w\left(1-\frac{w^2}{V^2}\right)\left(\frac{V^2}{w^2}-\tfrac{1}{2}\frac{V^3}{w^3}\log\frac{(V+w)}{(V-w)}\right) :$$

this is the increase in momentum per unit time, and therefore measures the force on the space inside the sphere. It will be noticed that this vanishes when $V=w$: thus a charged sphere, moving with the velocity of light through a magnetic field, will not be acted upon by any force. We may regard the force on the sphere as arising in the following way. Let us suppose that we have a uniform magnetic field parallel to y, then, in consequence of this external magnetic force, the closed tubes of electrostatic induction will be moving about in the field, the positive tubes going one way and the negative ones the opposite. Let us consider what happens when one of these tubes goes through the sphere. If β_1 and β_2 are the values of the magnetic force where it respectively enters and leaves the sphere, the momentum of the tube parallel to x when it enters the sphere is proportional to β_1, and when it leaves the sphere to β_2. Now β_1 and β_2 are different because on one side of the sphere the magnetic force due to the motion of the sphere acts in the same direction as the external magnetic force, but on the other side of the sphere it acts in the opposite direction. Thus the momentum of the tube parallel to x is not the same when it leaves the sphere as before it entered, so that the space inside the sphere must have gained or lost momentum.

The second case we shall consider is that of the magnetic field around a circular current of large radius. Then near a portion of this circuit, which we may consider straight, the tubes of electrostatic induction will be parallel to the circuit and moving radially, the positive tubes (*i.e.* those parallel to the direction of the current) moving inwards, the negative ones outwards : the positive tubes move in to the conductor and then contract in the manner previously described. The

motion of the positive tubes is the same as that given by Prof. Poynting in the Philosophical Transactions, 1884, part 1, p. 350.

In those parts of the field where there is no resultant electromotive intensity there will be as many positive as negative tubes in the field, and when the field is steady the positive ones will flow as fast in one direction as the negative ones in the opposite. Let us consider a region close to the circuit which we may here consider straight; let h be the sum of the strengths of the positive tubes in a unit of the area at right angles to the current, u their radial velocity, h' the sum of the strengths of the negative tubes, u' their radial velocity. Then in unit time the number of positive tubes flowing in plus the number of negative ones flowing out of any cylinder coaxial with the wire, must equal i the intensity of the current. If r is the radius of such a cylinder, the number of positive tubes flowing in in unit time is $hu \times 2\pi r$, the number of negative ones flowing out $h'u' \times 2\pi r$; hence we have

$$(hu + h'u)2\pi r = i.$$

But by equations (5)

$$4\pi(hu + h'u) = \beta,$$

if β is the magnetic force at the surface of the cylinder; as this is at right angles both to the direction of the tubes and also to their velocity, it will be tangential to the cylinder and at right angles to the current. From these equations we find

$$\beta = \frac{2i}{r},$$

the usual expression for the magnetic force close to a current.

The radial momentum inwards $= \Sigma h\beta = \beta\Sigma h$, hence the radial momentum carried across unit area of the cylinder in unit time

$$= \beta\Sigma hu,$$
$$= \frac{\beta^2}{4\pi}.$$

The electromotive intensity due to the motion of the tubes of electrostatic induction is

$$-\Sigma u\beta,$$

and is at right angles both to the magnetic force and the direction of motion of the tubes, so that in the neighbourhood of the current it will be parallel to the current. When the

field is in a steady state we have the positive tubes moving with equal velocity but in the opposite direction to the negative ones; in this case $\Sigma u = 0$, and there is no electromotive force due to the motion of the tube. When the current is first started the positive tubes move in before the negative ones begin to move out, so that in this case Σu is positive, and hence the electromotive force is negative, *i. e.* in the opposite direction to the current. When the current is suddenly stopped, the inward flow of tubes is stopped, but the outward one continues for some time; in this case Σu is negative and the electromotive force is therefore positive, *i. e.* in the direction of the original current.

We shall now consider, from the point of view of this theory, experiments such as those made by Rowland on the magnetic effects produced by the rotation of electrified disks. Let us consider a parallel plate-condenser rotating with an angular velocity ω about its axis, which we shall take as the axis of z. Let h be the electric displacement parallel to z; then the components of the magnetic force due to the motion of the tubes whose ends are on the plates of the condenser are given by

$$\alpha = 4\pi\omega x h,$$
$$\beta = 4\pi\omega y h,$$
$$\gamma = 0.$$

These values do not satisfy the solenoidal condition

$$\frac{d\alpha}{dx} + \frac{d\beta}{dy} + \frac{d\gamma}{dz} = 0.$$

So that inside the condenser we must have, in addition to the motion of those tubes which end on the plates of the condenser, a system of closed tubes in motion such that, while they do not alter the electric displacement, they alter the magnetic force. Thus we must have positive tubes moving in one direction and an equal number of negative ones moving in the opposite. If the motion of these tubes were confined to the inside of the condenser there would be no magnetic force outside the condenser, as the tubes of electrostatic induction outside are then all at rest, and it would follow that in this case there would be no magnetic force outside or inside. As this is not consistent with the results of Rowland's experiments, we shall suppose that these closed tubes pass right through the condenser, their motion being continuous from the inside to the out. The magnetic force due to the motion of these tubes will therefore be continuous as we cross the plates of the condenser. In consequence, however, of the

motion of the tubes which have their ends on the plates of the condenser, α and β increase respectively by $4\pi\omega xh$ and $4\pi\omega yh$ as we cross one plate and decrease by the same amount as we cross the other. Thus the conditions by which α, β, γ are determined will be that, except in the plates of the condenser, they are derived from a potential, that they everywhere satisfy the solenoidal condition, that γ is continuous, while α and β increase by $4\pi\omega hx$, $4\pi\omega hy$ respectively as we cross a plate of the condenser. Hence this distribution of magnetic force is exactly what would be produced if we supposed that each moving charge e of electricity produced the same effect as a current ωre, where r is the distance of the charge from the axis of rotation.

Hitherto we have only considered non-magnetic substances. We shall now proceed to discuss the differences which occur when the tubes of electrostatic induction are moving through iron or some other magnetic substance.

If a, b, c are the components of the magnetic induction, α, β, γ those of the magnetic force, the energy in unit volume is

$$\frac{1}{8\pi}(a\alpha+b\beta+c\gamma),$$

and if the magnetism is entirely induced and μ is the magnetic permeability, this equals

$$\frac{\mu}{8\pi}(\alpha^2+\beta^2+\gamma^2).$$

From this expression for the kinetic energy we can deduce the components of momentum and electromotive intensity due to a moving tube of electrostatic induction in the same way as we deduced equations (2) and (3). Doing so, we find for U, V, W, the components of momentum, the expressions

$$\begin{aligned} \mathrm{U} &= \mu(g\gamma-h\beta) &&= gc-hb, \\ \mathrm{V} &= \mu(h\alpha-f\gamma) &&= ha-fc, \\ \mathrm{W} &= \mu(f\beta-g\alpha) &&= fb-ga. \end{aligned}$$

And for X, Y, Z, the components of the electromotive force

$$\begin{aligned} \mathrm{X} &= \mu(\bar{w}\beta-\bar{v}\gamma) &&= \bar{w}b-\bar{v}c, \\ \mathrm{Y} &= \mu(\bar{u}\gamma-\bar{w}\alpha) &&= \bar{u}c-\bar{w}a, \\ \mathrm{Z} &= \mu(v\alpha-\bar{u}\beta) &&= va-\bar{u}b. \end{aligned}$$

Thus when a tube of electrostatic induction is moving with

the same velocity through places of given magnetic force, the momentum it possesses and the electromotive force it produces are proportional to the magnetic permeability of the substance through which it is moving. Hence the expressions for the mechanical force on a conductor conveying a current, and the electromotive force arising from electromagnetic induction, which we have deduced for non-magnetic substances, will be true for magnetic ones if we replace the magnetic force by the magnetic induction.

When the tubes are moving through a field partly occupied by iron, since the inertia of the tubes on the iron is very much greater than in the air, the flow of the tubes through the field will be affected by the iron in much the same way as the flow of a current of electricity would be affected if the air were replaced by a good conductor of electricity and the iron by a bad one.

We shall now consider some problems in which iron is in the field, selecting two-dimensional ones, as in these we avoid as much as possible purely mathematical difficulties.

Let us first take the case when an infinitely long cylinder whose axis is at right angles to the plane of the paper is introduced into a uniform magnetic field, the lines of force being parallel to the plane of the paper and horizontal. The tubes of electrostatic induction which are perpendicular to the plane of the paper were before the introduction of the iron moving vertically. When the bar is introduced they will avoid it, and will spread out so that their paths are like the lines of equipotential surfaces which are given for this case in plate xv. of Maxwell's 'Electricity and Magnetism;' the lines of magnetic force which are at right angles to the lines of flow of the tubes will therefore be the lines of force given in that figure.

Let us now consider the conditions which must be fulfilled at the surface separating iron from air in the general case when the field is not assumed to be uniform. If R is the velocity normal to this surface of a tube of strength h, then $\Sigma h\mathrm{R}$ must be continuous as we cross the surface, otherwise there would be an accumulation or the reverse of tubes at the surface. Now $4\pi\Sigma h\mathrm{R}$ is the tangential magnetic force; thus the tangential magnetic force must be continuous as we cross the surface. Again, the momentum parallel to the surface of a tube will not be altered as it crosses the surface. The momentum of the tube before crossing the surface is $h\rho$, if ρ is the normal magnetic force in air; after crossing the surface it is $h\mu\rho_1$, if ρ_1 is the normal magnetic force in the

iron : hence, since the tangential momentum is constant,

$$\rho = \mu\rho_1.$$

In other words, the normal induction is constant. Hence we have arrived at the usual boundary conditions for the lines of magnetic force.

The intensity of magnetization at the surface is

$$(\rho - \rho_1)/4\pi = \Sigma h(t - t_1),$$

where t and t_1 are the tangential velocities of the tubes in air and iron respectively.

That, from this point of view, magnetization corresponds to a discontinuity in the tangential velocity of the tubes of electrostatic induction.

We can easily prove from this consideration that if the lines of flow of the tubes coincide both inside and outside the cylinder with those due to a solid cylinder moving vertically through an incompressible fluid, the distribution of magnetic force will be that produced by the cylinder, if uniformly magnetized in the horizontal direction.

We have not hitherto determined the velocity with which the tubes of electrostatic induction are moving. We may, however, easily do this when the electromotive intensity is entirely due to the motion of the tubes. For, in this case X, the x component of the electromotive intensity, is given by the equation

$$\begin{aligned} \mathrm{X} &= \mu(w\beta - v\gamma), \\ &= 4\pi\mu\{w(wf - uh) - v(ug - vh)\}, \\ &= 4\pi\mu\{(u^2 + v^2 + w^2)f - u(uf + vg + wh)\}, \end{aligned}$$

with similarly expressions for Y and Z.
Since

$$\mathrm{X} = \frac{4\pi}{\mathrm{K}} f, \quad \mathrm{Y} = \frac{4\pi}{\mathrm{K}} g, \quad \mathrm{Z} = \frac{4\pi}{\mathrm{K}} h,$$

we see

$$u^2 + v^2 + w^2 = \frac{1}{\mu\mathrm{K}},$$

and

$$uf + vg + wh = 0.$$

Hence, in this case, the tubes are moving through the medium at right angles to themselves with the velocity of light.

XXII. *On the Measurement of Dielectric Constants by means of Hertz Oscillations.* *By* Ernst Lecher *.

THERE can be no doubt that the agreement demanded by Maxwell's theory between the dielectric constant and the square of the refractive index does not hold good in the majority of cases; and therefore, if we still wish to regard Maxwell's theory as true, disturbing secondary phenomena arise which alter the value of the dielectric constant as ordinarily determined. In the case of perfect insulators—whose number is, however, very small—a satisfactory agreement has already been found; but with less perfect insulators the discrepancies are very considerable. Now Schiller † has shown that for some substances the dielectric constants, measured with a very short time of charge, fulfil Maxwell's condition more nearly than in experiments with statical electricity. Moreover, the experiments and theoretical considerations of Cohn and Arons ‡ seem to point to an increase of dielectric constants with time of charge. The idea therefore suggests itself that the agreement with Maxwell's theory only holds for the case of an extremely short time of charge.

Starting with similar ideas, J. J. Thomson § has measured some dielectric constants by the aid of Hertz oscillations. More recently, without any knowledge of Thomson's work, I have carried out almost identical experiments. As, however, my results differ from those of Thomson, I venture to communicate them.

I found, to wit, that in the case of four substances which I investigated, the dielectric constant calculated from the capacity in the simple manner about to be described not only did not sink, but actually became greater, when Hertz oscillations were used.

Although I have used the term "dielectric constant," this is really not quite accurate. I have only compared capacities with each other, in which either air or the substance to be investigated was placed between the plates. Consequently in my results, in addition to dielectric action, we have conduction, residual charge, and other unknown errors creeping

* Translated from Wiedemann's *Annalen*, vol. xlii. p. 142 (Jan. 1891), by James L. Howard.

† Schiller, Pogg. *Ann.* clii. p. 535, 1874.

‡ E. Cohn and L. Arons, Wied. *Ann.* xxviii. p. 454, 1886, and xxxiii. p. 13, 1888.

§ J. J. Thomson, Proc. Roy. Soc. xlvi. p. 292, 1889.

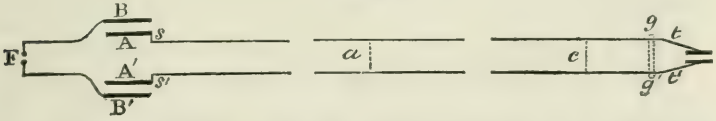
into the calculation. It might have been expected that these secondary effects, conduction, &c. would be entirely eliminated by the rapidly alternating charges of a Hertz oscillation; it appears, however, that even with such extremely short times of charge the secondary effects still increase the value of the dielectric constant, and indeed in a greater degree than before; provided, of course, that we assume the truth of Maxwell's hypothesis.

I have investigated two solid bodies, ebonite and glass, and two liquids, petroleum oil and water, by means of three different methods. The times of charge were 0·5, 5×10^{-4}, and 3×10^{-8} seconds respectively.

Experiments with Hertz Oscillations.

In a previously published paper on the study of phenomena of electric resonance *, I have already given a full investigation of all the conditions necessary in measurements by this method. In the present experiments exactly the same apparatus was used. In two parallel wires (fig. 1) *st* and *s't'*, 31 centim. apart, and each of length 1122 centim. (represented in the figure by broken lines), electric oscillations are excited

Fig. 1.



in a known manner by the oscillatory charging of condensers AB and A′B′ by means of a spark F. From the ends of the two parallel (leading) wires *t* and *t′* two flexible copper wires, each of length 69·7 centim., lead to two circular condenser-plates, each of radius R=9·68 centim.: these latter can be moved parallel to each other by the aid of a micrometer-screw. On bridging over the leading wires at certain places with a metal slider, the vacuum-tube *gg′* begins to glow. Every alteration of the capacity at the end of the wires displaces the ventral segment of the oscillation, and the slider must therefore be brought to a new position in order to make the tube glow once more.

I next measured very exactly the wave-length of a few oscillations with air alone between the condenser-plates. After this, the condenser-disks were screwed apart, and the substance to be investigated placed between them. By a few

* Lecher, Wied. *Ann.* xci. p. 850, 1890.

rough preliminary experiments the approximate relation between the position of the ventral segment and the distance apart of the plates was found, and then the position of the ventral segment was determined as accurately as possible for one or two of the distances found above. Thus, finally, in the two cases which I compared together, the fundamental oscillation was the same; the slider was in exactly the same position, only the distance apart of the condenser-plates at the ends of the wires was different, according as air or the substance experimented upon happened to be between them. Since in the two cases everything remained absolutely the same down to the capacities at the ends, I inferred that these capacities were also equal to each other, and thus the dielectric constant of the substance under examination (or rather the quantity to which this name is often erroneously given) could be determined in a simple manner.

If the space between the condenser-plates was filled with air we had, corresponding to distances apart of the plates,

0·791, 0·830, 0·870, ... 1·146, 1·186, 1·227, 1·266, 1·324, 1·360 centim.,

the following numbers as the mean distances of the ventral segment *a* from the end *s* of the wire,

641·48, 633·68, 629·18, ... 592·74, 586·72, 583·84, 580·35, 573·65, 570·54 centim. ;

and further, corresponding to an air-condenser with plates,

1·146, 1·186, 1·227, 1·266 centim.

apart, the mean distances of the ventral segment *c* from the end *s* of the wire were respectively

1045·74, 1043·70, 1041·73, 1038·64 centim.

The meaning of *a* and *c* is the same as in the paper on electric resonance previously referred to. The wave-lengths in the two cases are in the proportion of 1 to 2. For each distance apart of the condenser-plates, ten adjustments of the slider were made. After every measurement the slider was displaced by an assistant to such a distance that the vacuum-tube became quite dark, so that each new adjustment was found by drawing the slider along the wires with extremely great care. In spite of this, the greatest deviations amounted to 5–6 centim., but usually they were smaller than this. In

1800 adjustments which I have made altogether, there occurred on three occasions only a deviation from the mean value amounting to 5 centim.*

From these numbers I drew three curves, and endeavoured to bring the new ventral segment after the insertion of the substance under investigation within the limits just found, this being easily accomplished by suitably altering the distance between the condenser-plates.

Ebonite.—If a plate of ebonite, 0·7164 centim. thick, was placed between the condenser-plates, I obtained, corresponding to distances between the condenser-plates of 1·266 and 1·701 centim. respectively, for the ventral segment *a* the values 641·63 and 585·46 centim.; and for the ventral segment *c* corresponding to 1·701 centim. distance between plates, I obtained 1040·92 centim.

The thickness of the ebonite plate was measured by means of a micrometer-screw specially constructed for the purpose, and fixed in a brass frame. This brass frame was so large that the screw could be brought to any point on the dielectric. That portion of the ebonite plate which lay between the condenser-plates was divided up into squares, and the thickness of the ebonite was measured at the corners of these squares. The value given above is the mean of measurements taken at twenty different places; and Boltzmann † has shown that this mathematical mean is to be taken, within the limits of error, as the true thickness of the dielectric.

The first of the ventral segments just found, 641·63 centim., corresponds on the curve mentioned above to a separation of the condenser-plates of 0·791 centim., when air alone is between them. Therefore the capacity of the condenser, with plates 0·791 centim. apart and air only between them, is the same as that of the condenser with plates 1·266 centim. apart and the ebonite disk between them. The difference, 0·475 centim., represents the increase of thickness of the condenser in consequence of the insertion of the ebonite plate.

For the position of the second ventral segment, 585·46 centim., we had in the air-condenser a thickness of 1·206 centim., and after inserting the ebonite it became 1·701 centim. The difference is 0·495 centim.

For the third ventral segment, 1040·92 centim., we had in air a thickness of 1·234 centim. The difference is, in this case, 0·467 centim.

These three differences, 0·475, 0·495, and 0·467, should

* Some of the original measurements are given in full in *Wien. Ber.* xcix. pp. 483-486, 1890.

† Boltzmann, Pogg. *Ann.* cli. p. 568, 1874.

really be equal. Since the discrepancy follows no sort of rule either here or in later cases, and since the values are sometimes too great and sometimes too small, both for the ventral segment a and the ventral segment c, the latter of which corresponds to a vibration twice as rapid as the former, and finally seeing that there appears to be no definite relation between the discrepancies and the distance apart of the condenser-plates, we must attribute them to errors in the measurements, and most of all to the difficulty of moving the plates parallel to each other. The above agreement of the results with each other would, however, be fairly satisfactory; but it obviously becomes worse when we pass to the actual calculation of the dielectric constant; the deviation then becomes greater as the dielectric constant itself increases. In this and all other cases I take the mean of these differences and make use of it in determining the dielectric constant.

The mean of the three measurements given above is 0·479 centim. The value so calculated is subtracted from the thickness of the dielectric (0·716); this thickness, divided by the difference (0·237), gives the dielectric constant*. For ebonite, I thus obtain 3·01 as the value of the dielectric constant for such short times of charge as are measured by hundred millionths of a second.

The half wave-length of the shorter oscillation c was about 1000 centim.

* *Note by Translator*:—Perhaps the following will make the process of calculation more clear:—

Let C be the capacity of the condenser in each case, A the area of each of its plates. For the condenser with air alone let t_1 be the thickness of air (*i. e.* the distance between the plates). Finally, for the ebonite condenser of total thickness t_2, let there be a thickness t_2-e of air, and a thickness e of ebonite whose specific inductive capacity is κ.

Then

$$C=\frac{A}{4\pi\Sigma\left(\frac{t}{\kappa}\right)}=\frac{A}{4\pi\left(\frac{e}{\kappa}+t_2-e\right)}$$

for the ebonite condenser; and also

$$C=\frac{A}{4\pi t_1}$$

for the air condenser.

Hence

$$t_1=\frac{e}{\kappa}+t_2-e,$$

which gives

$$\kappa=\frac{e}{e-(t_2-t_1)}.$$

Glass.—If a glass plate 0·8797 centim. thick was placed between the condenser-plates I obtained, corresponding to distances between the plates of 1·582 and 1·954 centim., for *a*, the positions 634·57 and 587·54 centim.; and corresponding to 1·954 centim., I found for *c* the position 1042·74 centim.

These numbers were used in the same manner as the previous ones. The distance apart of the condenser-disks differs, according as the glass is inserted or not, by 0·758, 0·767, and 0·753 centim. The value of the dielectric constant is found to be 7·31.

Petroleum.—In order to bring a layer of liquid between the condenser-plates, I took a wooden ring whose internal diameter was 14 centim. On each face was fastened a thin glass plate, and thus a disk-shaped space was formed for the reception of the liquid. The thickness of the whole system was measured in thirty places, the liquid having been first inserted, in order to take account of the bulging produced by the pressure of the liquid against the sides of the vessel. The thickness of the two glass plates had also been previously measured in thirty places before cementing them on the ring. From these data the thickness of the liquid film could be calculated exactly.

If the two glass plates 0·4338 centim. thick were inserted between the condenser-plates, separated 1·590 centim., the ventral segment *a* was situated 583·93 centim. from the end of the wire; the same ventral segment corresponds to an air-condenser of 1·223 centim. thickness. The difference was 0·367. We obtain thus for the dielectric constant of the glass used ("Solinglas") 6·50, which number, however, may be less accurate than the others given in this paper, because the glass plates were too thin.

In order to obtain the dielectric constant of petroleum, I next found 571·93 for the ventral segment when petroleum and two glass disks were between the condenser-plates, these latter being separated by a distance of 2·848 centim. For the same ventral segment an air-condenser of thickness 1·348 centim. was required. The difference of these numbers 1·500 must be reduced by 0·367, which number, as shown above, expresses the effect of the two glass disks. After taking away the layer of petroleum alone, whose thickness was 1·9272 centim. (the glass disk still remaining in position), I had to diminish the distance apart of the condenser-plates by 1·133 centim. to make its capacity the same as before; and thus I obtain the value 2·42 as the dielectric constant of petroleum.

The petroleum used was the common commercial liquid as used for burning, and contained some water.

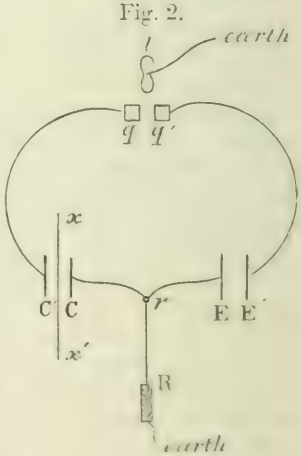
Water.—If I poured into the wooden ring distilled water (the thickness of the water alone being 1·9342 centim.), I found, with condenser-plates 3·160 centim. apart, a ventral segment *a* at 635·47 centim.

The difference calculated as in the case of petroleum gives in this case 1·953 centim. for a thickness 1·934 centim. of the dielectric. The error of experiment is therefore now too great, and if I wished to calculate the dielectric constant from these data as before, its value would be infinite.

Experiments with Ruhmkorff Oscillations.

In the determination of the dielectric constant by means of Ruhmkorff oscillations, I have adopted a method which is very convenient and simple and permits very exact measurements to be made. This method is in many respects similar to that used by Gordon *, but is much simpler. One pole of a small induction apparatus R (fig. 2) is put to earth: from the second pole one connexion is made to the condenser C and a second one to the comparison condenser E. The other two plates of these condensers, C′ and E′, are connected to the two quadrants q and q' of an electrometer by means of two parallel wires. The needle l of the electrometer is put to earth. The action of this arrangement is immediately seen. If the two condensers are equal, both quadrants are alternately charged and discharged in the same manner, and the needle remains at rest. If the one condenser is stronger, the electrometer-needle is momentarily deflected towards the corresponding quadrant.

Fig. 2.



The plate to be experimented on, xx', was then placed between the disks of the condenser CC′, and the other one EE′ (an ordinary Kohlrausch plate-condenser) was roughly adjusted. The final adjustment was made by the micrometer-screw of the con-

* G. Wiedemann, *Elektricität*, ii. p. 38, 1883. After this paper had been communicated to the Vienna Academy (16th May, 1890), the contemporary work of Donle was published (Wied. *Ann.* xl. p. 307, 1890). Our methods are almost identical, except that I use in place of an electrodynamometer an electrometer, which I consider in several respects more simple and advantageous.

denser CC′, this being the same condenser as I used for the previous experiments. The electrometer-deflexions were read by the aid of a telescope.

This method is surprisingly sensitive; the adjustments are very easily made, and moreover transient disturbances are easily recognized by the suddenness with which the effect appears; the raising of a hand, or a person passing, causes a momentary deflexion of the electrometer-needle *.

After the adjustment had been made with the plate xx' be- the condenser-disks, xx' was removed and then, without any alteration whatever in EE′, the plates CC′ were made to approach each other, until the electrometer-needle returned to zero.

In the following table the measurements have all been collected together. The numbers give the distance apart of the condenser-plates in centim., when the capacity has been kept the same, as described above.

	Ebonite (0·7164 centim.).		Glass (0·8797 centim.).		Petroleum + two glass plates (1·9272 +0·4338 centim.).		Water + two glass plates (1·9342 +0·4338 centim.).		Two glass plates (0·4338 centim.).	
With the dielectric .	2·1610	1·6090	2·6278	2·0325	3·6590	3·6560	4·2100	4·0035	1·8834	1·9240
With air	1·5785	1·0249	1·7240	1·1285	1·8120	1·8240	1·3410	1·1200	1·4401	1·4859
Difference	0·5825	0·5841	0·9038	0·9040	1·8470	1·8320	2·8690	2·8835	0·4433	0·4381

We thus obtain for the dielectric constant of

Plate Glass.	"Solinglas."	Ebonite.	Petroleum.	Water.
5·34	5·09	2·81	2·35	∞

These numbers are, apart from errors of the method, more exact than those of the previous section; the separate measurements by the next method show the least agreement.

* It should be noticed in passing, that if capacities are connected to C′ or E′ the alteration in the adjustment is considerable; if, on the contrary, a coil of wire be inserted in the conductor leading from C′ or E′ to the electrometer-quadrants the effect is smaller. The self-induction of the induction-coil is itself very large, the capacities on the contrary comparatively small. Of the disturbance introduced in consequence of damping the oscillations by causing the condenser-plates to approach each other, I shall speak later.

Experiments with a Statical Charge.

The arrangement is just the same as in fig. 2 of the previous section, except that a small influence-machine is used in place of the induction-coil. Its terminals were only separated by 0·05 centim., so that the sparks which passed and the potential differences were quite small. The one terminal was put to earth, and the other was connected for about 0·5 second with the point r. The adjustment and comparison of the two condensers took place exactly as before.

For water and petroleum no measurements could be obtained by this method, because in this case xx' acted as an earth-connected screen. In order to bring the needle to zero, I had to remove E′ to an infinite distance from E, so great was the conduction due to the small amount of water which the petroleum contained.

For the other substances, the measurements are given in the following table:—

	Ebonite (0·7164 centim.).		Glass (0·8797 centim.)		Two glass plates (0·4338 centim.).	
With the dielectric	1·5820	2·0640	2·4885	1·9820	1·8631	1·9942
With air.....	1·0090	1·4863	1·6150	1·1062	1·4330	1·5638
Difference	0·5730	0·5777	0·8735	0·8758	0·4301	0·4304

The corresponding dielectric constants are :—

Plate Glass.	"Solinglas."	Ebonite.
4·67	4·64	2·64

Synopsis of Results.

Collecting the results obtained by the three methods, in all of which high potentials are used, we find :—

Time of Charge in seconds.	Dielectric Constants of				
	Plate glass (0·8797 centim.).	"Solinglas" (0·4338 centim.).	Ebonite (0·7164 centim.).	Petroleum (1·9272 centim.).	Water (1·9342 centim.).
5×10^{-1}	4·67	4·64	2·64	Not measured.	
5×10^{-4}	5·34	5·09	2·81	2·35	∞
3×10^{-8}	7·31	6·50	3·01	2·42	∞

The dielectric constant, if we reckon it simply from the capacity as in this paper and as J. J. Thomson has done, is for quick oscillations not only not smaller, but, on the contrary, much larger. In all the substances investigated we have found the same phenomenon, and the differences found are too great for us to assume that they arise from secondary sources of error. I am therefore of opinion, contrary to J. J. Thomson, that in general we shall not be able to arrive at the true dielectric constant even by the aid of Hertz oscillations.

For the time of oscillation, neglecting certain terms which need not here be considered, we have

$$T^2 = LS(\lambda^2 + \pi^2),$$

where L is the self-induction, S the capacity, and λ the coefficient of damping. This damping (λ) increases as the oscillations become more rapid, and it is probable that in our Hertz oscillation the lag produced in the swing by damping is the chief cause of the increase which we have found in the dielectric constant. The phenomena taking place in the dielectric with such rapid oscillations are, however, in any case of too complicated a nature for me to advance this theory as an explanation of the increase of the dielectric constant with rapidity of oscillation *.

* That the phenomena are not so simple, and that in many cases, among which J. J. Thomson's experiments may also be counted, a decrease of the dielectric constant occurs with Hertz oscillations, is shown by the following experiments:—

The condenser-plates are separated by about 28 centim., and a trough of water 27 centim. long is placed between them. The capacity of this condenser, measured by my method with Ruhmkorff oscillations, is just the same whether the vessel contains distilled water, or water to which

For the majority of substances, then, an increase in the dielectric constant similar to that which I have found in the substances investigated might be expected; and it appears to me that in experimenting with slow swings there is more chance of success, since in that case, proceeding as Schiller or Cohn and Arons have done, the causes of error can be more easily eliminated from the experiments or allowed for in the observations.

Vienna, May 1890.

XXIII. *On the Flexure of a Flat Elastic Spring.* *By* Horace Lamb, *M.A., F.R.S.**

IT is a well-known consequence of the ordinary theory of flexure that when a bar of (say) rectangular section is slightly bent by opposing couples in a plane parallel to one pair of faces, so as to form a circular arc of radius ρ, the remaining faces take an anticlastic curvature σ/ρ, where σ is "Poisson's ratio;" and this fact has been made the basis of ingenious experimental methods of determining σ, by Cornu† and Mallock‡. It appears to have been first remarked by Thomson and Tait ('Natural Philosophy,' § 717) that this tendency to anticlastic curvature imposes in certain cases a limit to the degree of flexure, beyond which the theory in question will not apply. "For unless the *breadth* of the bar (or diameter perpendicular to the plane of flexure) be very small in comparison with the mean proportional between the radius [ρ/σ] and the thickness, the distances [in any cross section] from [a line through the axis perpendicular to the plane of flexure] to [one pair of corners] would fall short of the half-thickness, and the distances to [the other pair] would exceed it by differences comparable with its own amount. This would give rise to sensibly less

10 per cent. of sulphuric acid has been added. With Hertz oscillations on the other hand, the distilled water, used in the same trough, behaved as if it had a dielectric constant of about 300. If a few drops of sulphuric acid were then added to it, the oscillations either entirely ceased or at any rate were no longer visible by my method. The insertion of such thick layers would be of advantage, insomuch as one could compare the large dielectric constants not with air, but with a dielectric constant ∞. This mode of procedure cannot unfortunately be directly applied to Hertz oscillations, since the insertion of a conductor 27 centim. long alters the length of the path of the oscillations by too great an amount.

* From the Proceedings of the Manchester Literary and Philosophical Society, April 29th, 1890. Communicated by the Author.

† *Comptes Rendus*, August 2, 1869.

‡ Proc. Roy. Soc. June 19, 1879.

and greater shortenings and stretchings in the filaments towards the corners than those expressed in our formulæ, and so vitiate the solution. Unhappily, mathematicians have not hitherto succeeded in solving, possibly not even tried to solve, the beautiful problem thus presented by the flexure of a broad very thin band (such as a watch-spring) into a circle of radius comparable with a third proportional to its thickness and its breadth."

The difficulty thus arising in the case of a straight band, when the flexure exceeds a certain amount, makes its appearance *ab initio*, even for infinitely small changes of curvature, in the case of a band originally curved, and is in this way closely connected with the circumstance, first pointed out by Mr. Love*, that it is in general impossible to satisfy the boundary conditions for a curved plate or shell by a deformation such that the middle surface is absolutely unextended. In considering this latter question I had occasion, recently†, to work out the uniform flexure of a cylindrical plate, but I did not notice at the time that the same analysis, with the proper change of meaning of a coefficient, gives the solution of the problem proposed by Thomson and Tait. As the matter is of independent interest, and as so much importance has been attached to it by these writers, I take the liberty of reproducing the investigation (as suitably modified) in a separate form. The main results are such as might be anticipated from the above quotation. The extensions and contractions of the middle surface of the band, which are called into play by the tendency to the contrary curvature in the direction of the breadth, keep this curvature in check, so that the strained form never deviates appreciably from that of a cylinder. When the radius ρ is large compared with the third proportional aforesaid, the couple required to maintain the flexure has the value given by the ordinary theory; whilst in the opposite extreme it tends to the value appropriate to a *plate*. For intermediate cases we must have recourse to the general formula (18) given below.

Considering, then, a straight flat spring whose breadth $2b$ is large compared with the thickness $2h$, let us in the first instance suppose that by a proper application of force to the two ends (to be afterwards determined) it is bent so that the strained form is one of revolution. As regards the amount of the bending, we shall suppose only that ρ the radius of curvature of the medial line or axis, is large

* Phil. Trans. 1888(A), pp. 521, 524.

† Proc. Lond. Math. Soc. Jan. 1890. See also § 7 of a previous paper "On the Flexure of an Elastic Plate," December 1889.

compared with h. Let the band be divided into rectangular elements by two systems of normal sections respectively perpendicular and parallel to its length. The stresses across any section of the former system will reduce to a tension P, and a couple G, both reckoned per unit length; whilst across any section of the second system we shall have a tension Q, a couple H, and a shearing force Z in the direction of the normal. All these quantities are functions only of the distance (x, say) from the medial line. Considering the equilibrium of a rectangular element of breadth dx, and resolving parallel to x, we find

$$\frac{dQ}{dx}=0,$$

and since Q vanishes at the free edges, it follows that

$$Q=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

everywhere. Again, resolving along the normal, we have

$$\frac{dZ}{dx}-\frac{P}{\rho}=0;$$

and taking moments about a parallel to the medial line,

$$\frac{dH}{dx}-Z=0.$$

Hence

$$\frac{d^2H}{dx^2}-\frac{P}{\rho}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The remaining boundary conditions are evidently $H=0$, $Z=0$, that is

$$H=0, \quad \frac{dH}{dx}=0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The functions which occur in these equations have now to be expressed in terms of the deformation of the middle surface of the band. If a rectangular plate of thickness $2h$ undergo extensions σ_1, σ_2, parallel to the edges, the corresponding tensions are, per unit length,

$$\left.\begin{aligned} P&=\frac{4(\lambda+\mu)\mu}{\lambda+2\mu}(\sigma_1+\sigma\sigma_2).\ h \\ Q&=\frac{4(\lambda+\mu)\mu}{\lambda+2\mu}(\sigma_2+\sigma\sigma_1).\ 2h \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where λ, μ are the elastic constants of Lamé, equivalent to $m-n$ and n, respectively, in the notation of Thomson and Tait. If, further, the plate experience curvatures $1/\rho_1$ and $1/\rho_2$ parallel to its edges, the corresponding flexural couples are

$$\left.\begin{aligned} G &= \frac{4(\lambda+\mu)\mu}{\lambda+2\mu}\left(\frac{1}{\rho_1}+\frac{\sigma}{\rho_2}\right).\frac{2h^3}{3} \\ H &= \frac{4(\lambda+\mu)\mu}{\lambda+2\mu}\left(\frac{1}{\rho_2}+\frac{\sigma}{\rho_1}\right).\frac{2h^3}{3} \end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad (5)$$

Now let w denote the deviation at any point of the middle surface from the cylindrical surface (of radius ρ) drawn through the medial line, in the strained condition ; and let σ_0 be the extension of this medial line. We have evidently, in the present case,

$$\left.\begin{aligned} \sigma_1 &= \sigma_0 + w/\rho, \\ \rho_1 &= \rho + w, \\ 1/\rho_2 &= -d^2w/dx^2. \end{aligned}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The equations (1) and (4) show that

$$\sigma_2 = -\sigma\sigma_1,$$

and substituting from (4), (5), and (6), in (2), we get

$$\frac{h^2}{3}\frac{d^2}{dx^2}\left(\frac{d^2w}{dx^2}-\frac{\sigma}{\rho+w}\right)+\frac{1-\sigma^2}{\rho}\left(\sigma_0+\frac{w}{\rho}\right)=0.$$

An error of the order w/ρ in the values of the flexural *couples* is clearly unimportant*, so that we may write for the last equation

$$\frac{h^2\rho^2}{3}\frac{d^4w}{dx^4}+(1-\sigma^2)(w+\sigma_0\rho)=0. \quad . \quad . \quad . \quad (7)$$

The boundary conditions (3) give

$$\frac{d^2w}{dx^2}-\frac{\sigma}{\rho+w}=0,$$

$$\frac{d}{dx}\left(\frac{d^2w}{dx^2}-\frac{\sigma}{\rho+w}\right)=0,$$

or, by a similar approximation,

* This approximation may also be justified *à posteriori*. It wil appear that the terms neglected are of the order h/ρ compared with those retained.

$$\left.\begin{aligned} \frac{d^2w}{dx^2} - \frac{\sigma}{\rho} &= 0, \\ \frac{d^3w}{dx^3} &= 0, \end{aligned}\right\} \quad \ldots\ldots\ldots (8)$$

Let us write for shortness

$$m^4 = \frac{3(1-\sigma^2)}{4\ h^2\rho^2} \quad \ldots\ldots\ldots (9)$$

The proper solution of (7) is then

$$w + \sigma_0\rho = \mathrm{A}\cos mx\cosh mx + \mathrm{B}\sin mx\sinh mx\ ; \quad (10)$$

and the conditions (8) to be satisfied at the edges $x = \pm b$ give

$$\left.\begin{aligned} -\mathrm{A}\sin mb\sinh mb + \mathrm{B}\cos mb\cosh mb &= \frac{\sigma}{m^2\rho} \\ \mathrm{A}\,(\cos mb\sinh mb + \sin mb\cosh mb) & \\ +\mathrm{B}\,(\sin mb\cosh mb - \cos mb\sinh mb) &= 0 \end{aligned}\right\} \quad (11)$$

leading to

$$\left.\begin{aligned} \mathrm{A} &= -\frac{\sigma}{m^2\rho}\cdot\frac{\sin mb\cosh mb - \cos mb\sinh mb}{\sinh 2mb + \sin 2mb} \\ \mathrm{B} &= \frac{\sigma}{m^2\rho}\cdot\frac{\sin mb\cosh mb + \cos mb\sinh mb}{\sinh 2mb + \sin 2mb} \end{aligned}\right\} \quad (12)$$

The condition that $w=0$ when $x=0$ gives

$$\sigma_0\rho = \mathrm{A}, \quad \ldots\ldots\ldots (13)$$

and the value of w is thus completely determined.

The distribution of applied force and couple over the ends (supposed straight) necessary to produce the strain in question is given by

$$\mathrm{P} = \frac{8(\lambda+\mu)\mu}{\lambda+2\mu}(1-\sigma^2)h\,.\,\sigma_1$$

$$= \frac{2(3\lambda+2\mu)\mu}{\lambda+2\mu}h\left(\sigma_0 + \frac{w}{\rho}\right). \quad \ldots (14)^*$$

$$\mathrm{G} = \frac{8}{3}\frac{(\lambda+\mu)\mu}{\lambda+2\mu}h^3\left(\frac{1}{\rho} - \sigma\frac{d^2w}{dx^2}\right). \quad \ldots (15)$$

This distribution is somewhat artificial, but the theory of "local perturbations" developed by St. Venant, Boussinesq,

* Since $\sigma = \lambda\ 2(\lambda+\mu)$.

and others, warrants us in asserting that if it be replaced by any other distribution having the same force- and couple-resultants, the form assumed by the band will not be sensibly altered, except within a distance from the ends comparable with the breadth. It appears from (7) and (8) that

$$\int_{-b}^{b} \mathrm{P}dx = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

so that the forces on either end reduce to a couple

$$\int_{-b}^{b} \mathrm{G}dx = \frac{8}{3}\frac{(\lambda+\mu)\mu}{\lambda+2\mu}h^3\left\{\frac{2b}{\rho} - 2\sigma\left(\frac{dw}{dx}\right)_{x=b}\right\}. \quad . \quad . \quad (17)$$

On substitution from (10) and (12) this becomes, after a little simplification,

$$\int_{-b}^{b} \mathrm{G}dx = \frac{8}{3}\frac{(\lambda+\mu)\mu}{\lambda+2\mu}h^3 \cdot \frac{2b}{\rho}\left\{1 - \frac{\sigma^2}{mb}\frac{\cosh 2mb - \cos 2mb}{\sinh 2mb + \sin 2mb}\right\} \quad (18)$$

The form assumed by the cross section of the band, and the value of the flexural couple, depend on the magnitude of mb, which is comparable with $b/\sqrt{(h\rho)}$. For sufficiently small curvatures, *i.e.* so long as ρ is large compared with b^2/h, mb is small, and we find without difficulty

$$w = \frac{\sigma}{2}\frac{x^2}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

whilst the formula (18) for the flexural couple reduces to

$$\frac{4}{3}\frac{(3\lambda+2\mu)\mu}{\lambda+\mu}\frac{h^3 b}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which is in fact the value given by the ordinary theory for a bar of breadth $2b$ and depth $2h$, the coefficient $(3\lambda+2\mu)\mu/(\lambda+\mu)$ being Young's modulus.

As the curvature increases beyond the limit above indicated, the flexural couple increases in a greater ratio, until in the other extreme, when ρ is small compared with b^2/h, and mb is consequently large, the expression for the couple becomes

$$\frac{16}{3}\frac{(\lambda+\mu)\mu}{\lambda+2\mu}\frac{h^3 b}{\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)^*$$

the same as for a *plate*.

* This exceeds the value (20), given by the ordinary theory, in the ratio $1/(1-\sigma^2)$.

We have also in this case

$$\left.\begin{aligned} A &= \sqrt{2}\,\frac{\sigma}{m^2\rho}\,e^{-mb}\cos\left(mb+\frac{\pi}{4}\right) \\ B &= \sqrt{2}\,\frac{\sigma}{m^2\rho}\,e^{-mb}\sin\left(mb+\frac{\pi}{4}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (22)$$

approximately, so that the value of w given by (10) and (13) is insensible except close to the edges. Near the edge $x=b$ we have, for example,

$$w=\frac{1}{\sqrt{2}}\frac{\sigma}{m^2\rho}\,e^{-m(b-x)}\cos\left\{m(b-x)+\frac{\pi}{4}\right\}. \quad . \quad (23)$$

At the edge itself the deviation from the cylindrical form is comparable with h, but it rapidly diminishes as we pass inwards, at the same time fluctuating in sign. The latter result may perhaps be unexpected, but a little consideration will show that it is intimately bound up with the supposition we have made, that there is no resultant *force* on the ends of the band. The amplitudes of the fluctuations diminish, however, so rapidly that it is not likely that this feature of the strain could ever be made the subject of observation.

XXIV. *Specific Inductive Capacity of Electrolytes.* By Edward B. Rosa, *Fellow of the Johns Hopkins University* *.

[Plate VI.]

I. THE study of the specific inductive capacity of water and other conducting liquids was suggested to me about a year ago by Professor Rowland. Cohn and Arons and others had recently found values of K for water, ranging from 75 to 85 and for alcohol from 25 to 30; these exceeded so many times the value of K for most non-conductors that it seemed possible that there might be a relation between the conductivity and inductivity †; that these high values were directly due either to comparatively large conductivity, or

* Communicated by the Author. An abstract of this paper was read before the American Association for the Advancement of Science, Indianapolis, August, 1890.

† This seems to be a somewhat prevalent opinion. Thus, Andrew Gray ('Absolute Measurements in Electricity and Magnetism,' p. 491) says, referring to Cohn and Arons' determination of K for water and alcohol: "These substances have, however, considerable conductivity, which would tend, of course, to give an apparently high specific inductive capacity."

else both conductivity and inductive capacity were due to some common property of these liquids. In short, that the measured specific inductive capacities of conducting liquids were not genuine specific inductive capacities, the square roots of which, according to the electro-magnetic theory of light, should equal the corresponding indices of refraction, for waves of periods equal to those employed in measuring K. As will appear from the following pages, this anticipation has not been realized, the experiments indicating that these large values are true inductivities.

II. The method adopted for studying the question was to measure the force exerted between a fixed and a movable electrode in an electrolytic cell, varying the difference of potential of the electrodes, their distance apart, the periods of the alternating potentials employed, the temperature of the electrolyte, and its conductivity (the latter by varying the quantity of dissolved salts or other impurities). Water and alcohol are the electrolytes studied, and their behaviour has been compared with that of air, turpentine, and other dielectrics.

Apparatus.

The apparatus containing the electrolytic cell is shown in Plate VI. fig. 1. The movable electrode is suspended by a fine silver wire (·009 centim. in diameter) which conducts the current * to the electrode and whose torsion measures the force of attraction in question. The silver wire is attached above to the torsion-head *a*, and below at the mirror *c* to a thick wire which passes down into the liquid (contained in the glass dish *d*) ; then, bending at right angles, it forms an arm about 4 centim. long, at the end of which is attached the movable electrode, hereafter called the needle. Several forms of needle were used, but in order to secure a quick, nearly dead-beat motion, it was usually constructed of from two to five narrow plates above one another in horizontal planes, held together by vertical wires. The fixed electrode consists of a vertical plate of platinum, $3\frac{1}{2} \times 5$ centim. It is attached to a brass piece which slides in a slot in the ebonite plate *e*, and a graduated scale *s* permits the plate to be set at any desired point. All parts dipping into the liquid are made of platinum. A scale at a distance of three metres is seen by

* The current traversing this wire in the experiments was not sufficient to change its temperature as much as the ordinary fluctuations in the temperature of the room.

reflexion at the mirror c through a large reading-telescope. By means of a long wooden lever, attached to the torsion-head a and within reach of the observer at the telescope, the needle was always brought nearly to the same standard scale-reading when the force was acting upon it. This insured a constant distance between the needle and plate, and the amount of the deflexion was determined by taking the difference between this (nearly constant) deflected reading and the reading when the needle and plate are brought to the same potential. The distance (three metres) between the mirror and scale is sufficiently great so that the force may safely be taken as proportional to the scale-readings.

The disposition of the apparatus is shown in Plate VI. fig. 2. The difference of potential required is furnished by a gravity-battery, any desired value less than the whole potential being obtained by suitably manipulating the plugs of the resistance-box. The rotating-commutator is run by an electric motor. The commutator has two ebonite wheels, 10 centim. in diameter, mounted on a steel axle and carrying 2 and 26 segments of brass, respectively, with brass contact-brushes. Either wheel may be used and the speed varied through wide limits, so that the rate of alternation may have any desired value from a hundred to a hundred thousand per minute. Generally, however, the two-segment wheel was used, and the current reversed from 2000 to 4000 times per minute. A disk having 100 teeth, and gearing into the axle, served as a counter, and struck a bell every 100 revolutions. The potential was measured by a Weston voltmeter, inserted, as shown, between the resistance-box and commutator. It was carefully calibrated and, excepting an index error of 0·2 volt, was found correct as graduated. With respect to constancy and sensibility, this instrument has performed beautifully.

As soon as the brushes of the commutator came upon the insulating segments the electrodes would be discharged, wholly or in part, according to the conductivity of the medium. The electrodes were, therefore, short-circuited by a resistance (R', fig. 2) of about 16,000 ohms, and this insured a complete, instantaneous discharge for insulating as well as for conducting media. Thus the force acted on the needle for the same relative time in all cases, the circuit being broken for about $\frac{1}{25}$ of the whole time when using the two-segment wheel.

111. With this apparatus, during the months of May, June,

and July, a series of measurements of the force on the needle in different liquids was made, in which the following circumstances were varied in turn :—

1. Difference of potentials between the electrodes.
2. Distance between the electrodes.
3. Rate of alternations of the current.
4. Conductivity of the liquids.
5. Temperature.

1. *Variation of Potential*: *Turpentine, Water, and Alcohol.*— In the following tables the numbers in the third column are proportional to the squares of the potentials given in the first column, and the quotients of the deflexions by these squares (column 4) are constant within the limits of experimental errors. These nearly constant quotients are, however, slightly smaller in all cases for low potentials. This is doubtless due to the index error of 0·2 volt, which would be appreciable only in the case of the lower potentials.

TABLE I.—*Turpentine.*

Potentials, V.	Deflexions.	Squares of $\frac{V}{10}$.	Constant Quotients.
10 volts.	·10 cm.	1	·10
20	·41	4	·1025
30	·92	9	·1022
40	1·635	16	·1022
50	2·54	25	·1016
56·7	3·30	31·15	·1027

TABLE II.—*Water.*

Potentials, V.	Deflexions.	Squares of $\frac{V}{5}$.	Constant Quotients.
5 volts.	·35 cm.	1	·35
10	1·49	4	·37
15	3·51	9	·390
20	6·27	16	·392
25	9·93	25	·397
30	14·20	36	·394
35	19·15	49	·391
40	24·86	64	·389

TABLE III.—*Alcohol.*

Potentials, V.	Deflexions.	Squares of $\frac{V}{5}$.	Constant Quotients.
5 volts.	·11 cm.	1	·110
10	·48	4	·120
15	1·13	9	·125
20	2·03	16	·127
25	3·14	25	·126
30	4·45	36	·124
35	6·07	49	·124
40	7·91	64	·124
45	9·98	81	·123
50	12·39	100	·124
55	15·04	121	·124
60·75	18·45	147·6	·125

From these measurements it will appear that the force is accurately proportional to the square of the potential for these electrolytes as well as for dielectrics.

Low Potentials.—With the more sensitive instrument described below, measures of the force for lower potentials were made. By bringing the needle quite close to the plates (fig. 4) deflexions equal to those shown by the other instrument were obtained by forces 50 times smaller. Two causes tend to make the readings less accurate than before. First, since the electrodes are nearer, small inequalities in their distance produce a relatively greater effect. Second, the force is found to vary much more for low potentials with inequalities in the rate of alternation of the current. The following table shows, however, that the force is still proportional to the square of the potential :—

TABLE IV.—*Water.*

Potential, V.	Deflexions.	Squares of V.	Constant Quotients.
1·0 volt.	·75 cm.	1	·75
1·5	1·7	2·25	·76
2·0	3·0	4	·75
2·5	4·75	6·25	·76
3·0	6·5	9	·72
4·0	12·5	16	·78
5·0	20·0	25	·80

2. *Variation of Distance between Electrodes.*—In the following tables the readings of the deflexions were made in the order of the preceding numbers.

TABLE V. *Turpentine.*
[Constant potential of 50 volts.]

Distance between Electrodes.	Deflexions.			
cms.	cms.		cms.	
0·25			12	6·12
0·5	1	2·54	11	2·55
1·0	2	1·05	10	1·06
1·5	3	·60	9	·61
2·0	4	·40	8	·39
2·5	5	·27	7	·27
3·0	6	·21		

TABLE VI. *Alcohol* (temp. 22°·5.)
[Constant potential of 40 volts.]

Distance between Electrodes.	Deflexions.			
cms.	cms.		cms.	
0·5	6	19·53		
1·0	5	7·68	7	7·78
1·5	4	4·41	8	4·53
2·0	3	3·03	9	3·06
2·5	2	2·21	10	2·26
3·0	1	1·70	11	1·76

The plate cannot be set with anything like the accuracy with which the distance between needle and plate can be maintained constant, since the motion of the needle is magnified by the telescope and scale over a hundred times. Consequently the above measurements for variation of distance at constant potential are not as accurate as those previously given for variation of potential at constant distance.

If these measurements be plotted out with distances and deflexions as abscissæ and ordinates respectively, we get two curves resembling equilateral hyberbolas ; and if the ordinates of the alcohol curve be shortened eight times, the two curves will be almost indistinguishable. In other words, the rate of variation of the force with the distance between the electrodes is the same for turpentine as for alcohol (and water), and in general is probably the same for dielectrics and electrolytes.

3. *Variation of Rate of Alternation of Potentials.*—The effect of change of speed of the commutator is generally small and often inappreciable. With water the deflexion is greater at higher speeds, although for quite pure distilled water the difference is extremely small. For less pure water it is larger, although not often more than 2 or 3 per cent., and is probably due to polarization at the slower speeds. Not the slightest trace of bubbles appears on the electrodes when using moderately pure water, but with ordinary hydrant water at rather high potentials bubbles appear at all speeds. The needle is less steady at very low speeds, and when the commutator stops the deflexion changes considerably and is uncertain in amount except for very low potentials. It then depends also on the direction of the current. These phenomena were studied at some length, but as they seem to have no direct bearing on the present question, further reference to them is omitted.

4. *Variation of Conductivity.*—The resistance of different samples of distilled water is very different, and yet the difference noted in the force of attraction between the electrodes was relatively small. A single drop of a dilute solution of copper sulphate was added to a half litre of distilled water; the conductivity was increased about ten times while the force of attraction diminished about 15 per cent. Hydrant water, of comparatively large conductivity, showed a force 10 per cent. to 40 per cent. less than distilled, according to the potential, the effect of polarization being relatively greater at low potentials.

Thus, as far as the force of attraction depends upon the conductivity, it seems to be less as the conductivity is greater, and that because of polarization. Could the latter be eliminated in the case of these impure waters, the force would probably be practicably independent of the conductivity. Polarization reduces the force of attraction, as it reduces the current, in two distinct ways. First, by the counter-electromotive force excited which diminishes the effective fall of potential, and, second, by increasing the resistance at the electrodes. This decreases the current by increasing the total resistance; but it decreases the force not at all because of an increase in the *total* resistance, but because the additional resistance is introduced at one or two places and not uniformly throughout the liquid. The result is that the fall of potential is less in the liquid near the needle than before, and therefore the force on the needle is less.

The effect of introducing between the electrodes a stratum having a high resistance is strikingly shown in the following experiments:—

A.—A plate of mica (*m*, fig. 3, which is a horizontal section of the electrolytic cell) was inserted between the needle *n* and the plate *p*, and parallel to the latter. The following observations were made, the plate being set at distances from the needle given in column 3, the mica being in each case about 1·5 millim. from the platinum plate:—

TABLE VII.—*Water.*

No.	Potentials.	Distances.	Deflexions.	
1.	40 volts	1·0 cm.	+1·50 cm.	Without mica plate.
2	40 „	1·0 „	+ 0·84 „	With mica plate.
3.	40 „	0·55 „	0·00 „	„ „ „
4.	40 „	0·3 „	− 0·68 „	„ „ „

In numbers 1 and 2 the distance and potential are alike, but the force is eighteen times greater without the plate than with it. This cannot be explained by the simple fact that the specific inductive capacity of mica is perhaps a dozen times less than that of water, for that renders the equivalent thickness of water but a few millimetres greater, and so reduces the force by less than one half. On account of its comparatively large conductivity, however, the water on opposite sides of the mica quickly becomes charged as shown * (fig. 3), and the entire fall of potential just between the electrodes occurs in the mica. There is then no force on the needle in the direction of x, $\frac{dV}{dx}$ being zero. Around the edges of the mica plate, however, there is a fall of potential, and therefore a force, $\frac{dV}{ds}$, acting in different directions at different points on the needle. In (2) Table VII. the resultant of these separate forces is expressed by a deflexion of 0·84 centim. toward the plate. In (3) the resultant toward the plate is zero, while in (4), the plate being much nearer the needle, and therefore the lines of force curved backward to a greater degree, the force is apparently repulsive ; that is, the resultant is in the direction of $-x$.

B.—If now the fixed electrode be completely insulated instead of merely shielded by the mica, there is no appreciable force on the needle for the same difference of potential and rate of alternation used before. The 26-part wheel of the rotating commutator was substituted and the speed increased to 3000 per minute ; this gave 78,000 reversals per minute. The potential was increased to 75 and 90 volts, and a new apparatus arranged with two fixed electrodes and a larger double needle, as shown in section in fig. 4. The sensibility of this instrument was many times greater than the other, and enabled me to observe the very small force exerted on the needle, which it had been seen must exist when using insulated fixed electrodes and alternating potentials. For, just after each reversal there is a fall of potential in the water between the needle and the insulated plate, and therefore a force $\frac{dV}{dx}$ acting on each unit of electricity of the charged needle. This continues until $\frac{dV}{dx}$ is reduced to zero by conduction, which is accomplished in much less than a millionth

* The current is of course alternating, and so these charges as indicated in the figure are reversed perhaps fifty times per second.

of a second. During the remainder of the interval before the next reversal there is no force on the needle.

With 90 volts the deflexion was only a few millimetres, but the needle was perfectly steady, and readings were made to a tenth of a millimetre. For steady or slowly reversed potentials there was no perceptible deflexion, but above 10,000 reversals per minute the deflexion was perceptible, and increased to a maximum of 4·5 millim. at 78,000 per minute, the deflexions being sensibly *proportional to the speed*, as would be expected. This is therefore a very different case from that of uninsulated electrodes, where the force is many thousand times greater and practically independent of the speed.

C.—The secondary of a Ruhmkorff coil was substituted for the battery and commutator, and an alternating current sent through the primary. Comparatively large deflexions were observed with the same arrangement of insulated fixed electrodes. This was due to the much higher potentials, only an approximate estimate of whose value could be obtained. Owing to the nearly instantaneous character of the current from the Ruhmkorff coil, a far larger proportion of the effect observed with uninsulated electrodes would be observed with insulated.

D.—Since the small force on the needle observed with an insulated fixed electrode is due to the conductivity of the liquid, the same effect must occur, but in less degree, with liquids of less conductivity. To show this, two fixed electrodes, T and T′, were fastened, one to the inside and the other to the outside surface of the glass dish (fig. 5), and the latter filled with turpentine. The fixed electrodes are thus at nearly equal distances from the needle, and with rapidly alternating potentials the attraction was practically the same whichever was used. But for very slow alternations the force diminishes slightly, and for steady potentials falls to zero, when using the outer electrode, remaining practically constant for the inner electrode. In other words, when using the outer electrode and steady potential, the turpentine comes to a uniform potential by conduction, and the 95 volts fall of potential occurs entirely in the glass.

5. *Variation in Temperature.*—In order to determine the variation of the force with temperature, the apparatus (fig. 1) was set into a large glass jar, which was then filled with water up to the ebonite cover, *e*, or about a centimetre above the level of the liquid in the glass dish. The mirror remained in view above the top of the jar. Using hot water and ice as needed, the temperature of the water-bath was varied between

3° and 33° C., in a few cases being carried up to 45°. As soon, however, as the temperature rose much above that of the surrounding air, vapour condensed on the mirror and window before it, and thus rendered observations difficult or impossible. In every case, time was allowed for the temperature of the liquid (water or alcohol) to become nearly stationary before observations were made; otherwise convection-currents made the needle unsteady. However, it was not possible to keep the temperature perfectly steady, and the measurements, which are plotted out in Plate VI., figs. 6 and 7, are not so accurate and consistent as though made at one temperature. In the case of alcohol the needle was very unsteady above about 26°, and several rough measurements (Nos. 3, 4, and 9) made at higher temperatures are omitted from the diagram; but none are omitted below 26°, although Nos. 5 and 6 were somewhat unsteady. Ordinates represent temperatures, and abscissæ represent the excess of deflexions above 4·4 centim. in case of alcohol, and 8·0 centim. in case of water. The observations were made in groups in the order of the numbers on the diagram, and extended in the case of alcohol through a period of twelve hours. It will be noticed that the alcohol was carried several times through the given range of temperature; observations Nos. 2, 10, and 16 fall closely together near 25°, but between Nos. 2 and 10 the alcohol was cooled to 7°, and between Nos. 10 and 16 to 3° (see fig. 6). The observations fall upon a straight line as nearly as could be expected from the circumstances of the case. They indicate a rather large temperature-coefficient, the force falling off about 10 per cent. between 3° (5·20) and 26° (4·70). The conductivity, on the other hand, rapidly increases with the temperature, although no attempt was made to determine a value for its temperature-coefficient. According to Foussereau, the conductivity of alcohol increases nearly 30 per cent. between 3° and 26°.

In the case of water the observations do not lie as clearly upon one straight line, but the later observations are nearer to a second straight line nearly parallel to the first. This is believed to be due to polarization effects, which increased during the course of the day, the observations having extended over a period of 14 hours. However, the difference between the first and last measurements is scarcely more than one per cent., and the temperature-coefficient obtained from either or both combined will differ but little. The force falls off about 10 per cent. between 3° and 31°, a somewhat smaller change than with alcohol.

Assuming the specific inductive capacity to be proportional

to the force, we have the following expressions for the temperature-coefficients :—

$$\text{For Alcohol, } \frac{1}{K}\cdot\frac{dK}{dT} = -\cdot0046 \text{ for } T = 20^\circ\ C.$$

$$\text{For Water, } \frac{1}{K}\cdot\frac{dK}{dT} = -\cdot0038 \text{ for } T = 20^\circ\ C.$$

Values of K.

IV. The value of K for any liquid may be determined by taking the ratio of the force on the needle at a given distance from the fixed electrode for a given potential, the medium being the given liquid, to the force on the needle for the same distance and potential, the medium being air. Since the needle lies wholly upon one side of the axis of suspension, the latter is slightly displaced when the needle is immersed in a liquid, owing to the buoyancy of the liquid. This displacement is in a vertical plane passing through the centre of gravity of the whole suspended mass and the centre of gravity of the displaced liquid; and if this plane is not parallel to the plate, the distance between needle and plate will be thereby slightly altered. To avoid any error due to such a cause the needle was placed between two similar plates 15 millimetres apart, and the double deflexions noted as the needle was alternately joined to either plate, the other being at a different potential. The double deflexion was found to be constant for any position of the needle near the centre, so that no error could arise from small displacements due to the above cause. The results showed a slightly different value for the ratio sought than that found with a single plate, but the difference was so small that no appreciable error is believed to occur in comparisons of liquids, due to different specific gravities.

The needle was so constructed that in water, alcohol, or light oils it was nearly dead-beat while yet moving quickly. A brass weight attached just below the mirror rendered the suspension very stable, and when air-currents were excluded, the needle would take up a perfectly definite zero-position, to which it would usually return without a deviation of a thousandth of a millimetre. To render the needle equally stable and dead-beat in the air, a special damper (a vane of platinum hanging in oil) was attached in the axis of rotation. Diamond White headlight oil * was chosen as a favourable

* This is a high grade of refined petroleum.

liquid to compare with air, and to use as a standard of comparison with other liquids. The platinum damper was cut off after the comparison had been made, and the force on the needle in the oil was unaltered; thus no error was introduced by the presence of the damper. The following observations in detail are given as specimens to show the accuracy and uniformity in the measurements. The case of the oil is above, and that of the air below the average in these respects.

TABLE VIII.—*Air.*

Difference of Potential, 43·8 volts.

No.	Scale-Readings.		Differences = Double Deflexions.
	Centimetres.	Centimetres.	
1.	54·10		
2.		52·65	1·47
3.	54·13		
4.		52·65	1·48
5.	54·14		
6.		52·68	1·48
7.	54·17		
8.		52·69	1·48
9.	54·18		
10.		52·70	1·49
11.	54·19		
12.		52·70	1·49
13.	54·19		
14.		52·70	1·49
15.	54·19		
			Mean... 1·483

TABLE IX.—*D. W. Headlight Oil.*

Difference of Potential, 29·8 * Volts.

No.	Scale-Readings.		Differences = Double Deflexions.
	Centimetres.	Centimetres.	
1.	54·40		
2.		52·95	1·45
3.	54·40		
4.		52·95	1·45
5.	54·40		
6.		52·95	1·45
7.	54·40		
8.		52·95	1·45
9.	54·40		

* The voltmeter was kept at 44·0 and 30·0 respectively, but there is an index error of 0·2.

Following are the means of several such series, made in the order given :—

TABLE X.

No.			Double Deflexions.	
1.	D.W.H. Oil 29·8 volts.		1·450 cms.	
2.		Air, 43·8 volts.		1·482
3.		do.		1·473
4.		do.		1·472
5.	do.		1·438	
6.		do.		1·471
7.	do.		1·430	
8.	do.		1·436	
		Means	1·438	1·474

Each of the numbers given in the columns of deflexions is the mean of several separate measurements.

We have :—

$$\text{in air, } F = AkV^2,$$
$$\text{and in oil, } F_1 = AK_1V_1^2,$$

where F and F_1 are the forces in air and oil respectively, V and V_1 the potentials, A is a constant, K_1 = specific inductive capacity of the oil, and $k=1$.

$$\therefore \quad K_1 = \frac{F_1}{F} \cdot \frac{V^2}{V_1^2} = \frac{1{\cdot}438}{1{\cdot}474} \cdot \left(\frac{43{\cdot}8}{29{\cdot}8}\right)^2 = \mathbf{2{\cdot}11},$$

at 24° C., the *specific inductive capacity of Diamond White Headlight Oil.*

Water.

The means of three series of measurements of the force for 19·8 volts at 25° were 11·88, 11·80, 11·89. Mean = 11·86 = F. Mean for 44·8 volts in D. W. H. Oil = 1·69 = F_1.

$$K = K_1 \cdot \frac{F}{F_1} \cdot \frac{V_1^2}{V^2} = 2{\cdot}11 \times \frac{11{\cdot}86}{1{\cdot}69} \times \left(\frac{44{\cdot}8}{19{\cdot}8}\right)^2 = \mathbf{75{\cdot}7} =$$

specific inductive capacity of Water at 25° C.

The following is a list of several liquids with the corresponding values of K determined in this manner :—

Values of K *for Liquids.*

Water at	25° C.	75·7
Alcohol	25°	25·7
Sperm oil	20°	3·09
Benzine	21°	2·45
Turpentine, commercial	18°·6	2·43
"Neutral" petroleum ...	21°	2·26
D. W. Headlight oil ...	24°	2·11

Summary.

V. (*a*) The expression for the force between two electrodes having a homogeneous medium between them, thus forming a condenser, is of the form

$$F = AKV^2.$$

For a given liquid and given electrodes at a constant distance F is proportional to V^2. This is found to hold for electrolytes as well as dielectrics through the wide range of potentials employed.

(*b*) When the potentials and medium are constant and the distance between the electrodes varied, the value of F in the above equation varies in a manner sensibly independent of the nature of the medium, depending only on the capacity of the condenser.

(*c*) When the speed of the commutator changes, the force is but slightly altered, unless the electrolyte is a fairly good conductor. In the latter case the force is diminished as the speed is reduced, owing to polarization. There is a small change in the force with turpentine due to variation of speed, although none in the case of air. With turpentine, as with pure water and alcohol, the change is very small, the force being greater in every case with higher speeds.

(*d*) When the conductivity of distilled water is increased by adding hydrant water or minute quantities of acid or copper sulphate, the force is not greatly altered, although the current increases many times. The force, however, decreases, which is believed to be due to polarization. Were the latter wholly eliminated, the force would probably remain unaltered; at most it could differ but little.

(*e*) When the temperature rises, other circumstances remaining unaltered, the conductivity increases while the force decreases, the rate being constant or nearly so within the range of experiment. This decrease in the force, however, cannot be accounted for by polarization, for the increase of conductivity is not sufficient to make an appreciable difference in polarization effects. This is further proved by the fact that the force is immediately increased by a small decrease in the temperature, the curve returning upon itself, while if it were a case of polarization, the curve would more resemble the hysteresis-curve of magnetization.

VI. The almost complete agreement between the behaviour of the given electrolytes and that of dielectrics seems to show that the force acting on the needle is wholly independent of the quantity of current and of the conductivity of the medium, and it is difficult to conceive how the force and conductivity

can be due to a common cause or property of the liquid when their variations are so discordant in sign as well as in magnitude. This may be better seen perhaps by putting the expression for the force into mathematical form, and noting the consequences of the assumption that the force depends in some way upon the quantity of current.

Let us then assume that the large force of attraction observed in the cases of water and alcohol is the resultant of two effects, due respectively to the induction (which is proportional to the true specific inductive capacity) and the conduction or quantity of current passing; and that the second effect is large in proportion to the first. We may then write,

$$F = AKV^2 + ac, \quad \ldots\ldots\ldots \quad (1)$$

where F = the resultant force on the movable plate of the condenser,
V = the difference of potential between the plates,
K = the true specific inductive capacity,
A = a constant depending on the geometry of the condenser,
c = the current,
a = an undetermined coefficient.

We may write equation (1) as follows:—

$$F = AKV^2 + \beta V, \quad \text{or} \quad \frac{F}{V^2} = AK + \frac{\beta}{V}.$$

Now experiment shows (see Tables II., III., IV.) that $\frac{F}{V^2}$ is constant for a given liquid, and hence β is either zero or proportional to V. Suppose it is not zero. Then

$$F = AKV^2 + \beta_1 V^2, \quad \ldots\ldots\ldots \quad (2)$$

or

$$F = AKV^2 + a_1 c^2. \quad \ldots\ldots\ldots \quad (3)$$

Thus the second term, if it is not zero, is proportional to the square of the current; a_1 being an undetermined coefficient.

Now we have for the case of a homogeneous medium between the plates of a condenser the following equations:—

$$C_1 = \frac{Q}{V} = -\frac{K}{4\pi V} \int\int \frac{dV}{dn} dS, \quad \ldots\ldots \quad (4)$$

$$\frac{1}{R} = \frac{c}{V} = -\frac{\kappa}{V} \int\int \frac{dV}{dn} dS, \quad \ldots\ldots \quad (5)$$

where C_1 is the capacity of the condenser whose medium has a specific inductive capacity K; and $\frac{1}{R}$ is the conductivity

of the condenser, the medium having a specific conductivity κ.

$$\therefore \quad \frac{C_1}{\frac{1}{R}} = \frac{K}{4\pi\kappa}, \text{ or } \frac{1}{R} = \frac{4\pi\kappa C_1}{K} = 4\pi\kappa C_2,$$

where C_2 is the capacity of the condenser with air as dielectric. Neglecting polarization effects, which in these experiments were usually negligible, equation (3) becomes

$$F = AKV^2 + a_1 \frac{V^2}{R^2},$$

or

$$F = AKV^2 + a_1 (4\pi\kappa C_2 V)^2. \quad . \quad . \quad . \quad . \quad (6)$$

For convenience we may take the case of a guard-ring condenser, in which case the value of A is $\frac{2\pi C_2^2}{S}$, S being the area of the disk. Then equation (6) becomes

$$F = \frac{2\pi}{S} C_2^2 V^2 \left\{ K + a_1 b \kappa^2 \right\}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $b = 8\pi S$, a constant numerical factor. a_1 is our undetermined coefficient; we only know of it that it is independent of V. We should expect it, however, to be a constant, at least for a given liquid. By assumption, $a_1 b \kappa^2$ is large compared with K, so that any considerable change in F would be due chiefly to a change in $a_1 b \kappa^2$.

Experiment shows that when C_2 is altered by varying the distance between the plates, $\frac{F}{C_2^2}$ is constant. Hence a_1 is independent of C_2.

When a very small quantity of acid or salt is added to the liquid, κ is increased—in a particular case about ten times. F was found to be but slightly altered *. Therefore, since κ^2 was increased 100 times, a_1 must have decreased 100 times, $a_1 \kappa^2$ remaining constant. We have thus found that a_1 is independent of V and C_2, and is inversely proportional to κ^2.

When alcohol is heated from 3° to 26°, the force falls off 10 per cent (see fig. 6). But, according to Foussereau †, κ in this case increases about 30 per cent., or κ^2 69 per cent. We know that the change in F due to change in K is small, when K is small compared with $a_1 b \kappa^2$. Hence a_1 is no

* This assumes that the observed diminution was chiefly due to polarization, which is very probable.

† *Journ. de Physique*, 1885.

longer inversely proportional to κ^2, but decreases more rapidly than κ^2 increases.

Thus the conditions which the function α_1 must fulfil are not only what we should not expect, but are actually inconsistent. Turning now to the other alternative, namely, that β is zero (and therefore α and α_1 are zero), we have the force expressed by $F = AKV^2$, an expression which applies equally to dielectrics and electrolytes. In both cases K is independent of A and V, as we have seen. It changes little if any with a variable conductivity, but changes notably with the temperature. The only other determinations of temperature-coefficients which I have seen are those of W. Cassie *, made at the Cavendish Laboratory. He worked with a number of solid and liquid dielectrics, for the most part between about 15° and 50° or 60° C. Here are his mean values of $\frac{1}{K}\frac{dK}{dT}$:—

Solids.		Liquids.	
Mica	+·0003	Turpentine . .	−·0011
Ebonite . . .	+·0004	Carbon bisulphide	−·0040
Glass . . .	+·0012	Glycerine . . .	−·0056
,, . . .	+·0020	Benzoline . . .	−·0011
		Benzine . . .	−·0013
		Olive oil . . .	−·0024
		Paraffin oil . .	+·0023

We notice that the solids and paraffin oil have positive coefficients, while all the other liquids have negative coefficients, like water and alcohol. Further, the values of the temperature-coefficients for water and alcohol are not only of the same order of magnitude as those for the given liquid dielectrics, but both (−·0038 and −·0046) fall within the limits of the series, water having a value less than carbon bisulphide and glycerine and greater than turpentine, benzoline, benzine, and olive oil.

VII. It is very convenient to think of the force acting on the needle as due to a given charge tending to flow down a given slope of potential. Letting $\frac{dV}{dx}$ represent the resultant slope of potential, the displacement over the surface of the needle is $A_1K\frac{dV}{dx}$, A_1 being a constant depending on the needle, and K a constant depending on the medium. One can just as readily imagine this displacement occurring in a conducting as in a non-conducting medium. Indeed, Maxwell

* Proc. Roy. Soc. vol. xlvi. (1889), p. 357, and Phil. Trans. 1889.

says * that this inductive capacity probably exists in all bodies †. The capacity of a condenser consisting of two electrodes immersed in a conducting medium cannot be measured by discharging its accumulated charge through a galvanometer, and noting the deflexion of a magnetic needle. But it is as directly measured by noting the force which this constant (but continually renewed) charge exerts as it tends to flow down a given slope of potential. The conductivity of water depends mainly, if not wholly, upon its impurities, which form in the case of distilled water an indefinitely small part of its bulk. The inductivity, on the other hand, is a property of the water itself, and hence ought not to be appreciably modified by small quantities of foreign substances, though it might be greatly different if they constituted a large part of its bulk. We may thus think of conduction and induction producing their separate effects side by side, the former not affecting the latter. Conduction may, however, affect the force $A_1K\left(\frac{dV}{dx}\right)^2$ by modifying $\frac{dV}{dx}$ through polarization, not by changing K.

That Maxwell's criterion of the equality of the specific inductive capacity to the square of the index of refraction is so far from being fulfilled in the case of water and alcohol, is not a serious objection to the notion that electrolytes possess a real specific inductive capacity. For comparatively few substances is $K=n^2$ within the limits of experimental error. Glass among solid and castor oil and ether among liquid dielectrics are notable exceptions. These are usually explained by supposing that the electrical displacements in these dielectrics are much greater in a second or even a millionth of a second than they would be in periods of 10^{-15} sec., a thousand million times shorter, such as the period of light. J. J. Thomson ‡ has recently shown that for periods of 4×10^{-8} sec. the value of K for glass is very much nearer to n^2 than for longer periods, and there is good reason for believing that K for periods equal to those of light-waves

* Electricity and Magnetism, vol. i. p. 53.

† It is scarcely necessary to point out that the habit of reckoning the specific inductive capacity of metals as infinite when calculating the "reduced thickness" of the stratum between the plates of a condenser does not at all imply that if metals have a specific inductive capacity it must be infinite or even large. Because of their conductivity there is an instantaneous distribution of electricity such that there is no fall of potential in passing through the plate of metal; and this is what would happen if the metal had an infinite specific inductive capacity and zero conductivity.

‡ Proc. Roy. Soc. vol. xlvi.

would equal n^2. The electrical behaviour of glass has been compared with the mechanical behaviour of pitch, which is elastic to forces acting through short periods such as those of sound, but viscous to forces of long periods. If we accept this very reasonable explanation for glass, we at once extend it to the large class of liquids of various degrees of insulating power called dielectrics, and for which K is greater than n^2, and also to that group of alcohols and their derivatives which Tereschin* has investigated, and for which the values of K vary from 2 to 32. It is but another step to water with a value of K in the neighbourhood of 75. One can easily imagine that for electrical stresses of a period 10^{-15} sec. K can equal n^2; that is, be less than 2, and possess a temperature-coefficient equal to that of n^2.

That a thing is conceivable and that it is demonstrated are not equivalent. Nevertheless the behaviour of water, alcohol, and other conducting liquids, as cited in the foregoing pages and as given by other observers, seems to me to afford very strong reasons for attributing to these electrolytes a *genuine specific inductive capacity*.

This investigation was carried on under the general direction of Prof. A. L. Kimball, of the Johns Hopkins University. The experiments were made at the Physical Laboratory of the University of Wisconsin; and I take pleasure in acknowledging my obligation to Prof. J. E. Davies, who generously placed at my disposal the utmost resources of his laboratory, and who furnished me with the beautiful rotating commutator which was constructed from my design in the University machine-shops.

Johns Hopkins University,
Baltimore, Dec. 20, 1890.

Note, *added January* 14, 1891.—It is well known that a dielectric in a non-uniform electric field tends to move toward regions where the force is greater or less (like magnetic and diamagnetic bodies in a magnetic field), according as the specific inductive capacity of the body is greater or less than that of the medium in which it is placed. For example, if the body is glass (K = 6 to 10), it will tend to move toward places where the force is greater in such media as air and other gases and in turpentine, oils, and most liquid dielectrics. But in alcohol, water, and other liquids having larger specific inductive capacities we should expect it to move in the opposite direction.

* Wied. *Ann.* Bd. xxxvi. S. 792 (1889).

Experiments upon which I have been engaged since the above paper has been in type fully confirm these expectations. Preliminary measurements show that the force with which the glass suspended in water tends to move toward the weaker parts of the field is several times greater than that with which it tends to move toward the stronger parts of the field in air, and that, other things being the same, this force is proportional to the square of the electric force.

A conductor, on the contrary, tends to move toward the stronger parts of the field *for all media*, with a force many times greater in water than in air or oil. Increasing the conductivity of the water does not appreciably alter the force.

A new piece of apparatus is being constructed, and when finished accurate measurements will be made of the force on the suspended body in these several cases. The preliminary results are of interest, however, as confirming the conclusions of the foregoing paper that water and other conducting liquids have a true specific inductive capacity.—E. B. R.

XXV. *Experiments in Photoelectricity. By* GEORGE M. MINCHIN, *M.A., Professor of Mathematics in the Royal Indian Engineering College, Coopers Hill*.*

NEAR the beginning of the year 1877 I commenced a long series of investigations in Photoelectricity, and I was not then aware that M. Becquerel had previously worked at this subject and had obtained some results which I also obtained independently. In the spring of 1880 I made a verbal communication to this Society, illustrated by experiments, on the generation of electric currents by the action of light on silver plates which were coated with collodion and gelatine emulsions of bromide, chloride, iodide, and other salts of silver, as well as with eosine, fluorescine, and various aniline dyes. A short summary of these results appears in the Report of the meeting of the British Association that year at Swansea. The chief object which I had then in view in prosecuting such experiments was the solution of the problem of producing a photographic image of an object at a distance by means of an instrument which is still imaginary and which I proposed to call a *telephotograph*.

As these experiments have never been published in adequate detail, I propose to begin this paper with an account of them.

* Communicated by the Physical Society: read January 16, 1891.

Silver Plates.

Let two strips of cleaned silver foil be each fastened on a plate of glass, by means of pitch or other suitable substance; take some finely powdered chloride of silver and shake it up well in a test-tube containing collodion, the emulsion being, of course, screened from light by a covering of black paper on the test-tube; pour a thin coating of the emulsion over both silver plates in the dark; and when the films have set, immerse both plates in a glass vessel containing distilled water with a few grains of common salt; screen one plate completely; and then connect the plates with the terminals of a Thomson galvanometer. A disturbing current will, of course, be produced; but if the plates are very nearly alike, this current will be small and will soon almost disappear.

Now, on exposing the unscreened plate to light, a current will be produced, and the exposed plate is *negative* to the unexposed (*i. e.*, as copper to zinc).

The direction of the disturbing current is not in any way related to the direction of the current produced by light—as is, indeed, *à priori* evident.

If the plates are coated with an emulsion of bromide of silver, the liquid being distilled water with a few grains of bromide of potassium, the exposed plate is made also *negative* with respect to the unexposed by the action of light.

If the plates are coated with iodide of silver by first pouring a layer of iodized collodion over them, and then immersing them in a nitrate of silver bath, the liquid being water with a few grains of iodide of potassium, we obtain a reversal of the nature of the exposed plate; *i. e.* the action of light makes the exposed plate *positive* with respect to the unexposed.

By placing coloured glasses in front of the exposed plate in each of these cells, it was found that the red rays produced comparatively feeble currents, while the currents produced by the blue and violet rays were very great; but the directions of the currents were the same for all rays.

A somewhat different result was obtained when the plates were coated with an emulsion of sulphide of silver, the liquid being water with a few grains of sulphate of potash. The exposed plate is, as in the case of iodide of silver, *positive*. In this cell the directions of the currents were the same for rays passing through all the coloured glasses; but the strength of the current was very much less for rays passing through the green glass than for the rays at each side of the green.

When the plates were coated with an emulsion of nitrate of silver and gelatine, the water containing a few grains of

nitrate of barium, the exposed plate was positive, the effect of the red rays being exceedingly small and that of the blue very great.

Photographic Effect of the Current.—A fact of very great importance in this subject is that which relates to the action of an electric current which passes through a photographic layer on a plate.

Two silver plates, each coated with a film of Liverpool emulsion (bromide of silver), were immersed in a tumbler containing distilled water and a few grains of bromide of potassium. One of these plates was connected with the zinc and the other with the carbon pole of a bichromate cell. The current was allowed to pass through the plates for a few seconds, with the following results:—

(1) The plate connected with the carbon pole was, without the employment of any developer, visibly blackened in its immersed part.

(2) No *visible* change took place on the other plate; but when the plate was developed, by pouring over it the usual pyrogallic acid developer, its immersed portion was also blackened.

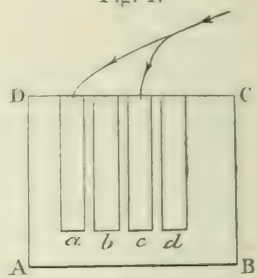
The photographic result was also obtained when the bichromate cell, which originated the current, was replaced by a photoelectric cell exposed to light. A vessel containing distilled water and a small quantity of bromide of potassium was placed in a dark room; in this vessel were immersed (or partially immersed) two silver plates S′, V′, the first coated with a film of Liverpool emulsion, the second uncoated. These plates were connected by insulated wires with the plates, S, V, of a glass cell containing water and a small quantity of common salt, the plate S being coated with a layer of a chloride of silver emulsion, and the plate V being uncoated. Magnesium light was then allowed to fall on the plate S of this latter cell for a few minutes. Now, whether S′ was connected with S or with V, the plate S′ when taken out of the vessel and developed was very sensibly blacker on its immersed portion than on the unimmersed. The action on the plate S′ was assisted by exposing it for about ten seconds to gaslight before the photoelectric current of the exposed cell was passed through it. The effect is undoubtedly due to the action of the current, because when the plate S′ was left immersed in its cell for twenty hours and then developed, no blackening effect was produced.

Not only is this photographic effect of the current important, but it is also important to prove that the effect on a sensitized plate is strictly confined to those portions of it

through which a current passes; and to establish this fact more fully the following experiment was made :—

On a glass plate, ABCD, were cemented, close together but not in contact, several strips of silver foil, *a*, *b*, *c*, *d*, . . ., the whole plate being uniformly coated with a film of Liverpool emulsion ; two or more of the silver strips, *a*, *c*, were put into the circuit of a bichromate cell, the other strips, *b*, *d*, being left out of the circuit. This glass plate with its strips was half immersed in a vessel of water in presence of another silver plate, and the current was passed for a few seconds. On removing the sensitized plate from the vessel and applying the developer, the blackening took place only on those strips which were metallically thrown into the circuit, *and only on the immersed portions of those strips.*

Fig. 1.



I made use of this principle in an attempt to transmit an image of a simple figure to a distance ; but the arrangements were so difficult that the success attained was small, and I must leave the matter for renewed trial.

Eosine.—Comparatively strong currents are obtained by coating a silver plate with an emulsion of eosine and gelatine, and the currents are strengthened by allowing the film to set thoroughly on the plate. But such a plate has the drawback that the eosine readily leaves the film and comes into the liquid. This passage of the eosine may be delayed by pouring a layer of collodion over the dry gelatine film. By the action of light, this plate is rendered *negative* to the unexposed plate.

When daylight was allowed to fall on this plate, any variation of the light caused by a passing cloud, or the interposition and withdrawal of the hand in front of the cell, was at once accompanied by a variation of the current strength ; and the same thing is true for all the cells previously described ; but no variations of sufficient rapidity are produced to affect a telephone, although the make and break of the current itself is, of course, amply sufficient to do so.

The photographic action on a bromide-of-silver plate placed in a cell in a dark room and connected with one of the poles of an eosine cell was effected by the current generated by daylight in the latter without any preliminary exposure of the bromide plate to gaslight.

A very curious case of *inversion of the current* produced by

light was observed in a cell containing eosine in solution; and as the same effect was occasionally observed in cells of other kinds employed in experiments made long afterwards, I shall draw attention to the phenomenon here.

Two clean silver plates were immersed in a glass cell containing distilled water and a very small quantity of eosine. One of these plates was screened and the other exposed to light, both being connected with the galvanometer. Immediately on exposure of the plate to light, there was generated a current in which the exposed plate was *positive* to the other. This current, however, lasted for only a second, and it was then (the exposure continuing) succeeded by a steady and much stronger current in the opposite direction, this latter being the current which would exist if the plate had been coated with an eosine-gelatine film in the usual way, any variation in the intensity of the light being answered by a corresponding variation in the strength of the photoelectric current. Now when the light was suddenly shut off from the plate, the instantaneous effect was to *increase* the existing current—the effect being merely impulsive—after which (the plate being screened) the current gradually disappeared. This result was again and again reproduced, and exactly the same result was found if the water in the cell contained a small quantity of fluorescine instead of eosine, except that the initial and final impulsive currents were much smaller with fluorescine than with eosine.

The plates of this cell having been left in the liquid and kept in the dark for a fortnight, the action of light was again tried; and it was then found that, while the inverse currents were produced as before, the initial current on exposure was enormously increased both in magnitude and in duration. It now disappeared gradually, and was succeeded by a current in the reverse direction.

When one of these plates was removed from the cell and immersed in water in presence of a clean silver plate, it was at once, on exposure to light, *negative*, like a silver plate coated in the ordinary way with an emulsion of eosine.

M. Becquerel, in the course of his experiments on the electric action of light on plates coated with salts of silver, made the observation that in the case of *silver* plates coated with bromide, chloride, and iodide of silver, the nature of the exposed plate (whether positive or negative) depends on the *thickness* of the layer deposited on the surface of the plate. Thus, he says (*La Lumière*, vol. ii. p. 129):—"By depositing on one of these plates a *thin* layer of iodide, obtained by the action of the vapour of iodine at the ordinary temperature,

and then exposing this plate to light, it was found that it took *positive* electricity from the liquid. . . . . With a *thick* layer of iodide on the surface of the silver, there is, on the contrary, a current the inverse of the preceding ; that is to say, the plate exposed to light took *negative* electricity. This result shows that, in this case, iodine acts on silver under the influence of light." He then gives a table of deflexions obtained when various coloured glasses were placed in front of a silver plate coated with a thick layer of iodide, the greatest effect being produced by violet rays, and the least by red, the former being 22 times the latter.

M. Becquerel continues :—" Thus, whilst with chloride and bromide of silver precipitated, placed on plates of platinum, there is always produced a current of the same sense, the exposed plate being positive, with a layer deposited on silver, there is an effect depending on the thickness of this layer. These two inverse effects indicate that there should be necessarily a thickness for which the electric effect is almost nothing."

These observations of M. Becquerel may possibly explain the above inverse effects in the eosine-silver cell ; but his last conjecture would not be practically verifiable, unless, when the critical thickness was reached, the state of the sensitive surface was one of stability. One result, however, would pretty evidently follow, viz., that if on the same plate a portion of the layer was below the critical thickness, while the remainder was above it, the plate, on exposure, might be, on the whole, positive, negative, or inert. In the case of photoelectric cells to be subsequently described, it is possible that the observed results are due to this cause.

Certain mordants were tried for the purpose of preventing the eosine from leaving the film. The sensitized plate was washed with a solution of borax, which had the effect of keeping the film on the plate, but almost completely destroyed its sensitiveness to light. A similar effect followed from the employment of a solution of chloride of aluminium. The best effect was produced when a silver plate coated with an emulsion of eosine and photographic gelatine was immersed for a few minutes in a strong solution of alum.

Naphthalene red, a substance soluble in alcohol and only slightly soluble in water, was also used in place of eosine. A little of this was dissolved in alcohol and then emulsified with gelatine. It was then poured on a silver plate, and the film was allowed to set thoroughly. The photoelectric currents produced were not quite so strong as those obtained with eosine. The effect is much greater in the blue than in any

other part of the spectrum, the exposed plate being positive; and, apparently, with strong red rays, there is a reversal of the sign of the E.M.F.

Various other substances were used, among which I may mention iodine green, which gives rather strong currents with daylight, the exposed plate being negative.

In all these cells the E.M.F. is feeble compared with the electromotive forces which I have obtained by other means, to be presently described; but in the case of silver plates coated with iodine green, an E.M.F. of about $\frac{1}{20}$ volt can be observed with sunlight.

Fluorescine used like eosine on silver or platinum plates gives poor results.

A few experiments with a solution of sulphate of quinine and some other fluorescent liquids were made with a view to connecting fluorescence with electric effect; but the observed results were comparatively small, and the subject has been left for further trial.

Other Metals.

Many experiments were made with other metals, but the currents produced by most of them were smaller than those given by silver plates. Thus, I have on record an experiment in which bismuth was melted into thin plates which were fixed on glass, and then immersed in a cell containing water. When light fell on one of these plates, a considerable current was generated, the exposed plate being positive; but on adding a solution of chloride of bismuth to the water, the current generated by light was reversed. On taking them out of the cell and washing them with distilled water, and then immersing them again in a water-cell, when the plate was exposed to light, there was an impulsive current corresponding to a negative nature of the plate, but this was promptly succeeded by a very large current in the opposite direction—just as in the cases previously mentioned.

Copper, antimony, and other metals were also tried, but the results are not of sufficient importance to demand any detailed record. In particular, iron plates coated with the magnetic oxide and immersed in water yielded photoelectric currents.

Tin Plates.

A glass cell containing a solution of fluorescine in distilled water, in which two silver plates had been immersed, was taken for trial with other than silver plates. Almost the first metal that I used in this cell was tin. Two plates of tin foil whose surface had not been in any way prepared,

but which was in the state in which it was obtained from the manufacturers, were fixed on plates of glass and placed in the cell. One of them being screened from light and the other exposed, a very strong current was the result. When the tin plates were replaced by copper, a current, but of less strength, was also produced. Gold plates gave no current at all. It was found, however, that the fluorescine was unnecessary, and that when common tap-water was used in the cell, the currents produced by light seemed to be no weaker than before. If the hand or any other screen were moved rapidly in front of the exposed plate, the spot on the galvanometer-scale moved correspondingly. A telephone was put into the circuit with a view to the production of sound by variations in the incident light, but the alterations were not sufficiently rapid to produce this result. A battery of three cells in series was then formed, but no sound was produced in the telephone, and, moreover, the current indicated by the galvanometer was no greater than when only one cell was used. This latter fact seemed most extraordinary ; but, on examining the cells separately, I found that one of the cells was producing a current in a sense opposed to that of the current given by the other two. Of this more presently.

When the liquid in the cell was distilled water, currents were still produced by the action of light on the tin. When a drop of sulphuric acid was added to the water, the currents ceased.

In nearly every cell that I used with tin plates—whose surfaces, as stated above, had not been treated in any way—the exposed plate was *positive* to the unexposed ; but, after a time varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed plate was *negative*. Thus there was a change in the sign of the E.M.F. produced by the continuous action of light. This again reminds us of M. Becquerel's observation about the thickness of sensitive layers. There seemed to be almost no exception to the rule that the exposed plate begins by being positive and ends by being negative, the negative regime lasting for many days of prolonged exposure to light.

It was also found that when the chloride of any substance was dissolved in the distilled water of the cell, all photoelectric action ceased. Again, if the tin foil is cleaned by immersion in sodic hydrate and then in hydrochloric acid, or by immersion in a solution of either of the chlorides of tin,

the plate becomes completely insensitive to light. Thus the photoelectric result is obviously due to some layer on the surface.

In connexion with the change of sign of the E.M.F. produced by continuous exposure, the following remarkable experiment was made. Round the outside of a cylindrical porous pot was fixed a coating of tin foil; inside the pot was placed a strip of tin foil, these two strips being the exposed and unexposed plates of the cell respectively. The porous pot was filled with water and immersed in a glass beaker also containing water, the diameter of the beaker being very slightly greater than that of the porous pot. The strip of foil inside the pot was completely covered from light and connected with one terminal of a galvanometer; the foil outside the pot being connected with the other terminal. Outside the glass beaker, and fitting round it very closely, was a cylinder of black paper with a vertical slit cut in it, the breadth of the slit being about half an inch, while the diameter of the cylinder was about 3 inches. Thus, by rotating the black paper cylinder round the beaker, different strips of the tin foil on the outer surface of the porous pot could be successively exposed to light.

The slit in the paper occupying a given position, the corresponding portion of the tin foil was exposed to sunlight. The current indicated that the plate was positive, and the exposure was continued until the current changed its direction, *i. e.*, the plate became negative. The slit was then moved opposite another and distant portion of the tin foil, which, by the same process, was finally rendered negative; and so on all the way round. Thus the surface of the tin foil was divided into a number of strips, which were alternately negative and positive in their electromotive forces when exposed to light; and by rotating the black paper continuously round the beaker, a series of currents in contrary directions were obtained from the action of light on one and the same metallic plate—a result which, at first sight, sounds very strange. It is easily understood, however, when we remember the different conditions into which the various strips of the surface of the plate—*i. e.*, some very thin stratum on the tin—were put in the preliminary process; and, moreover, it prepares us for cases in which different portions of a tin plate which has been sensitized by a special process give, on exposure, electromotive forces of different signs.

I have not yet spoken of any process for producing a sensitive layer on the surface, and a long time elapsed before I discovered one. The tin foil hitherto spoken of is pure

tin foil as it is obtained from the maker; and, as must be expected, not only were some pieces on exposure to light observed to be at once negative while others (the great majority) were positive, but there were various degrees of sensitiveness. Occasionally, also, the curious jerks immediately on exposure and immediately on screening, which were observed in the case of silver and eosine, were observed with these plates.

Then succeeded a series of experiments in which a quadrant electrometer was used instead of the galvanometer, *i. e.*, the E.M.F., and not the current, was measured.

A curious result was very soon observed with the thin tin foil which is wrapped inside small packages of tobacco. The two sides of this foil are notably different in appearance, one being somewhat dull, while the other has a bright silvery aspect. Two strips of this were cemented on opposite sides of a small glass plate, the dull surface of one and the bright surface of the other being fixed to the glass. This plate was immersed in a glass cell containing absolute alcohol, the two pieces of tinfoil being connected with the poles of the electrometer. When the bright surface was exposed to daylight, a small deflexion was obtained which showed the plate to be negative; when the dull surface was exposed, the deflexion was more than doubled, the plate being, like the other, also negative, and the magnitude of its E.M.F. being about $\frac{1}{16}$ volt.

A tin-foil plate, which at once on exposure to light is negative, is produced by thoroughly cleaning a piece of foil and coating it with *sulphide* of tin, either by exposing it to SH_2 or by rubbing a little "mosaic gold" over the surface.

When distilled water was used instead of alcohol, the E.M.F. produced by light was in all cases diminished; *and the same result always happened when any salt whatever was dissolved in the alcohol with a view to diminishing its resistance.*

This unfortunate result is characteristic of every photoelectric cell that I have employed. It is unfortunate, because it seems to preclude the possibility of obtaining really strong and practically useful *currents* by the action of light, and it appears to indicate some essential connexion of *resistance* and *electromotive force.*

The liquid is, of course, an essential element of the cell, and a very large number of liquids was tried in these experiments. Thus, for example, the two tobacco-foil plates when immersed in peroxide of hydrogen were absolutely insensitive. The alcohols are much the best liquids when tin

plates are used. Large electromotive forces have been obtained with all of them; but they are not all of quite equal value. As has been already stated, if any substance containing chlorine is put into the liquid, the E.M.F. of light completely ceases.

If a small quantity of nitrate of potassium is dissolved in the alcohol, a Thomson high-resistance galvanometer will be very easily and strongly affected by the photoelectric currents of these cells.

Among liquids an aqueous solution of pyrogallic acid is one which presents itself as worthy of trial, since pyrogallic acid is a greedy absorber of oxygen; and I have on record a striking result of its employment. A small plate of tin foil, the surface of which had been cleaned, was covered over with a thin layer of water, with which a drop of nitric acid had been mixed; the foil was placed on a glass plate, under which was applied a gas-flame until the liquid had quite evaporated, and the tin foil remained coated with some salt of tin. Whatever this salt was, when this plate was immersed in a cell containing absolute alcohol in presence of a cleaned tin-foil plate, the first was, on exposure to light, strongly *negative* to the second. The sensitive plate was then taken out of this cell and immersed in another containing a clear aqueous solution of pyrogallic acid. It was now absolutely insensitive to light. Taken out of this cell, and dried with blotting-paper, it was again put into the alcohol; and now, on exposure to light, it was found to be strongly *positive*. Here, then, is a case of complete reversal. This change was accompanied by a slight jerk or kick in the E.M.F., such as has been already described in connexion with silver and eosine; that is, on exposing the plate for the second time in alcohol, the initial indication of the electrometer was a very slight kick indicating a negative E.M.F., but this was immediately followed by a large deflexion in the opposite direction. This result was repeated many times; the plate was taken out of the alcohol and dried in the dark for about two hours, and when replaced in the alcohol cell the jerk and large contrary deflexion were obtained.

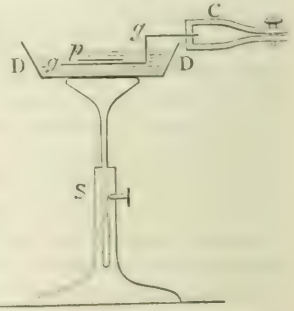
A similar experiment has been recently tried with a tin-foil plate sensitized by the process which I now adopt, and which will be presently described, and the result obtained was not the same as the above. In the new process the plate *appears* to be coated with the white oxide of tin, SnO_2; but whether it really is so or not, I cannot say. However, such a plate which had been in a cell with methyl alcohol for two years was taken out, together with the back or unexposed plate,

and immersed in a cell with an aqueous solution of pyrogallic acid. On exposure to light in this cell, the plate was about half as sensitive, and of the same sign (positive) as in the methyl alcohol ; and on replacing it in the alcohol cell, its indication was less than it had been originally. Thus, there was merely a falling off, but not an absolute destruction, of the E.M.F. caused by the pyrogallic acid, the sensitive surface having assumed a yellowish appearance.

The conjecture of M. Becquerel, that the sign of the E.M.F. developed by light depends on the *thickness* of the sensitive layer on the plate, has been already mentioned ; but it may be allowable to put forward another conjecture—that when there are two, three, or any number of salts of a metal, any one of which may be on the plate, the result depends on the particular salt, and that the series may be alternately positive and negative on exposure to light according to the amount of oxygen (suppose) that they contain. A reducing agent may convert one of these into an adjacent one, and so alter the sign of the E.M.F. The question is not one with which I am competent to deal ; it is for the chemist. And it might also be worth while to investigate whether there is any connexion between the sign and magnitude of the E.M.F. generated by the action of light on a metallic salt and the effect produced on the salt by electrolysis.

Production of the Sensitive Surface.—After trying a very great number of processes for producing a sensitive tin surface which is *positive* on exposure to light, the following is that which I have found to be most efficacious.

Fig. 2.



Take a strip of *pure* tin foil, say 1 inch long and $\frac{1}{8}$ inch broad, and about as thick as a stiff sheet of note-paper (the very thin foil is not suitable ; but the exact thickness is not of much consequence) : clean it first in sodic hydrate, and then in dilute hydrochloric acid, or in hydrofluoric acid, until the surface presents a bright crystalline appearance. Having thoroughly washed it in distilled water until every trace of acid disappears from the water, place it horizontally, at p, on a bent plate of glass of the shape $g\,g$ in fig. 2, this plate of glass being held by a clamp C supported by an ordinary retort-stand, which is not represented in the figure ; under the tin plate p and the

glass place a dish, D D, supported by a stand S, which allows the dish to be raised or lowered; the dish being raised until it nearly touches the glass g, pour into it, until the tin plate p is completely covered, a portion of the following mixture :—

500 c. c. of distilled water,
3 c. c. of pure nitric acid,
15 grammes of nitrate of ammonia.

If the tin *is pure* and has been *thoroughly cleaned*, the moment the plate p is covered by the solution, a whitish deposit is thrown down on its surface. The plate may be left in the solution for 3 or 4 minutes, and then the dish D D is lowered and removed. The deposit on the tin should be uniform and must not be allowed to form for more than 4 minutes. When the dish D D has been removed, the under surface of the glass plate g g should be dried by blotting-paper. Then a process of heating must take place. The flame of a spirit-lamp must be applied uniformly to the under surface of the glass plate, *i. e.* moved backwards and forwards until the whole of the liquid on its upper surface is evaporated. Great care must be taken not to melt the tin plate p

Continuing the heating process, the upper surface of the tin passes through a series of appearances. At first (*i. e.*, when the water has just been evaporated) the deposit has a dull slaty look; as the heating goes on, this changes to a whitish aspect, a gas with a nitrous smell coming off; as the heating is continued, this whitish surface undergoes a rapid change to a dark colour with, apparently, a tinge of green, which travels like a shadow from one end of the plate to the other; the heating being still continued, this dark surface changes to a strong white, and the flame ought to be kept under it until the gas is completely driven off.

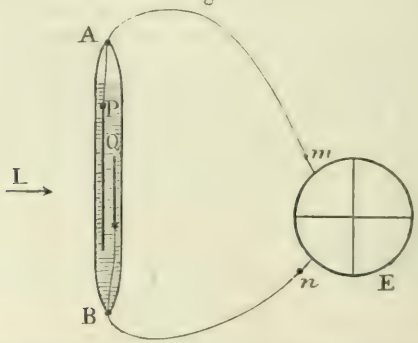
The plate should then be plunged into alcohol. It is now in the most sensitive condition. I have found that if the heating is stopped at the end of the penultimate stage—viz., that in which the dark greenish colour has been reached—the plate will be very fairly sensitive to light. It may be suspended from a platinum wire fixed through a pin-hole at one end of the plate, and when placed in an alcohol cell in front of a clean tin plate similarly suspended, these plates being connected with the poles of an electrometer while the cell is screened from light, a small difference of potential will be observed, the sensitized plate being positive to the unsensitized; but this difference of potential will usually disappear after a short time.

Many liquids can be used in the cell; but I have found that the best results are obtained from *methyl alcohol prepared from oil of wintergreen*. With methyl alcohol prepared from wood-spirit I failed to obtain anything like the maximum E.M.F. on exposure to light. A plate so prepared is, on exposure to light, positive to the clean plate in the cell. In some liquids the plate is almost quite insensitive to light, but on replacing it in methyl alcohol its sensitiveness reappears.

It is remarkable that the plate while immersed in the cell (and unexposed) takes a considerable time—about five hours—to develop its maximum sensitiveness; that is, the cell should be left in the dark for this time to allow the plate to develop. Moreover, shortly after the plate has been formed, it is much more rapid in its response to light and shade than it is subsequently; not that there is any falling off in the final indications of E.M.F., but that the indications are more slowly produced.

Fig. 3 represents a cell connected with the electrometer. AB is a small glass tube nearly full of the liquid; P and Q are the sensitized and unsensitized plates, two fine platinum

Fig. 3.



wires being either soldered to them or passed through minute holes in them, these wires being sealed into the glass tube at A and B, and connected with the poles m, n, of a quadrant electrometer, E; the arrow L represents the incident light.

After forming the sensitive plate, it should be tried in the cell before the cell is sealed up completely; if it is not satisfactorily sensitive, it should be taken out and re-heated either on the glass plate in fig. 2 or over the chimney of a paraffin lamp. This further heating will often convert a partially sensitive plate into a very sensitive one.

The cell is usually fixed in a piece of cork by means of which it may be held in a support.

Dispersion of the Residual Effect.—On the withdrawal of the light, the fall of E.M.F. in the cell is usually much slower than the rise of E.M.F. on exposure ; and this fact would constitute a grave inconvenience if there were no speedy remedy. The effect of the light can, however, be quickly and satisfactorily overcome by connecting the exposed plate with the copper, and the unexposed with the zinc pole of a Daniell cell for a few seconds—the time of connexion being longer as the time of exposure of the plate to light was longer. In fact, a series of three or four impulsive contacts with the poles of the Daniell, followed by a few seconds' short-circuiting, will suffice to remove the residual effect of light, and to leave the spot on the electrometer-scale at the point from which it started.

This result is important, because when feeble light, such as that of a candle, falls on the cell, the maximum E.M.F. takes some minutes to develop, and the return of the spot on the scale would occupy a long time.

Variation of the Effect with the Distance of the Source of Light.—Six cells connected in series were placed on circles of varying radius, and a candle was in each case placed at the centre of the circle. The E.M.F. developed by the light of the candle was, with fair accuracy, found to be inversely proportional to the distance of the candle from the cells. As the intensity of the light varies inversely as the square of the distance, it follows that the square of the electromotive forc is proportional to the intensity of the light.

Curve of Rise of E.M.F.—The law of increase of E.M.F. during exposure was studied by placing a "standard" candle at a distance of 6 inches from 6 cells connected in series, the poles of the series being connected with a Thomson quadrant-electrometer. The deflexions on the scale were noted every quarter minute, and a curve was traced having the deflexions for ordinates and the times for abscissæ. The maximum E.M.F. attained was ·566 of that of a Minotto cell, giving for each cell ·094 of this amount.

If we denote by A the maximum E.M.F. developed, and by η the E.M.F. at any time t, it would appear to be legitimate to assume the equation

$$\frac{d\eta}{dt}=k(\mathrm{A}-\eta),$$

where k is a constant. This gives, by integration,

$$\eta=\mathrm{A}+\mathrm{B}e^{-kt},$$

where B is another constant. The curves actually traced in

the experiments closely satisfy an equation of this form, which is, of course, that of a logarithmic curve.

The curve of fall is probably of the same nature, but the rate of fall is much slower than that of rise, as is evident by an inspection of the diagram exhibited to the Society.

Unhomogeneous Surfaces.—To produce a homogeneous surface on the sensitive plate, it is manifestly necessary to satisfy two conditions: the deposit produced by the oxidizing solution must be uniform, and so must the heating by the spirit-lamp. It is obvious, then, that if these conditions are not fulfilled, we must be prepared to find some part of the plate positive and another part negative on exposure to light; and such has actually been found to be the case in many experiments. But a much more extraordinary result of quite common occurrence is that described under the next head.

Impulsion-Cells.—It often happens that, a few days after a cell is mounted and found to be duly sensitive to light, an exposure produces no E.M.F. at all. But if a slight tap (sometimes scarcely audible) is given either to the support of the cell or to the table on which this support rests, a change, indicated by the motion of the spot on the electrometer-scale, takes place in the cell, and it is as sensitive to light as it was originally. Another tap given to the base throws the cell again into the insensitive state; another tap will restore the sensitive state; and so on indefinitely.

These results are not due to any defect in the contact of the platinum wires with the plates; these wires are tightly pinched to clean parts of the plates, and often soldered to them.

It might be conjectured that these results are due to the formation of some gas in the cell; but how can one tap replace the gas which has been displaced by another tap?

I believe the sensitive and insensitive states to be due to some molecular alteration, either in the sensitive surface or in the liquid, or in their layer of contact—a sort of polarity in the medium which, as in the case of magnetic bodies, can be produced or destroyed by vibrations. Thus the E.M.F. due to light may be simply due to strain and not accompanied by any actual chemical combination.

A most remarkable instance of these impulsion-effects may be cited to show that they are not due to any defective contact. Referring to fig. 3, which represents the sensitive plate completely submerged in the liquid, let the plate be only partially submerged, and let the liquid surface be at a point C, about midway between B and A, the portion CA of the cell being occupied by vapour alone. This will be the state of

affairs in a cell which was under experiment. It was found that on exposing the upper portion, CP, of the plate and screening the lower, a *negative* deflexion on the scale was observed—that is, a deflexion which indicated that the exposed plate was negative ; while if the upper portion was screened and the lower exposed, a *positive* deflexion resulted. Then on giving a slight tap to the support of the cell and exposing the portion CP, while screening the lower, a *positive* deflexion was observed ; and on exposing the lower portion alone, a *positive* E.M.F. resulted, as before. Thus the effect of the vibration was to alter the nature of the upper portion while leaving the lower unaltered.

In another cell, which I now exhibit to the Society, the sensitive plate was completely immersed, and there was, as in the last case, a certain portion, CP, at the upper end which was rendered alternately positive and negative by vibrations, while the lower portion remained unaltered. These facts seem to be quite inconsistent with a want-of-contact theory. Before citing another experiment, in which a Thomson galvanometer is employed, to disprove such a theory, it is well to mention a remarkable method of producing the sensitive state from the insensitive.

While investigating the effect of static charges communicated to the plates on the sensitive and insensitive states, I found that if a Voss machine, not in any way connected with the cell or the electrometer, was worked in the room while the cell was in the insensitive state, *the moment a spark passed between the poles of the Voss, the insensitive state was altered to the sensitive*, whether the cell was connected with the electrometer or not. The same effect was produced at a much greater distance from the cell by the inductive action of the spark passing between the two poles of the secondary coil of an induction-coil, as in a Hertz oscillator arrangement. In fact when a Hertz oscillator was taken into the grounds outside the laboratory in which I worked, the induction-coil being actuated by a battery of 4 or 5 Grove cells, no wires whatever passing from this machine near the laboratory, the insensitive cell inside the room at a distance of 81 feet was instantly rendered sensitive by the inductive action of the Hertz arrangement.

Impulsion-cells differ much from each other in the readiness with which they undergo the change from one state to the opposite ; but the most obstinate can be thrown from the insensitive into the sensitive state by leading a wire connected with either pole into the vicinity of a Hertz or a Voss machine.

I am not able to produce the reverse effect—the change from the sensitive to the insensitive state—by electromagnetic induction; dull taps administered to the base of the cell constitute the only way in which this change can be produced with certainty. On very rare occasions the change has been effected by the inductive action of strong sparks from a Leyden jar; but the result is quite exceptional. There appears to be some reason for supposing that this change—from sensitive to insensitive—is produced by vibrations of slow period, or very dull taps. I have produced it by dropping very small pieces of cork on the base of the iron retort-stand in which the cell is held, and even by gently drawing a piece of paper across the retort-stand.

Nearly all these tin-foil cells will develop the impulsion character a few days, or weeks, after they have been formed, *provided that the alcohol in them has not been thrown out and replaced by fresh alcohol.* Three years ago I formed a battery of 30 of these little cells, testing each before adopting it in the battery, and connected them in series, hoping thereby to obtain a very large E.M.F. on exposure to light. To my disappointment, however, I found a comparatively small result; and on examining the cells individually, I found some of them insensitive. Their sensitiveness was restored by renewing the alcohol, but it might have been restored by impulses if I had known the fact.

One of this battery in which the impulsion results appeared was taken out and its alcohol renewed on 4 or 5 days successively, with a view to ascertaining whether the impulsion results could be got rid of by renewing the liquid. After six renewals the cell ceased to give impulsion-effects, and it has been since under trial from time to time for about three years.

Impulsion-cells are very strongly influenced if they are kept in a room in which powerful sparks are being produced from a Holtz machine. A box of them which had been put by, for exhibition before this Society, in a cupboard about six feet distant from a Holtz which was put in action, was found during the process to have had nearly every cell affected in such a manner that no impulsion-effects could be produced for several hours after the Holtz ceased to be worked; and a strikingly good example of an impulsion-cell which I was very anxious to preserve acquired a strong tendency to revert from the sensitive to the insensitive state, and to remain in the latter; at the same time it lost its extreme sensitiveness to impulses.

The experiment with a galvanometer, previously men-

tioned, to show that in neither state of an impulsion-cell is there a want of contact, is as follows:—An impulsion-cell in which both plates hang from the top of the cell, and in which the liquid did not rise nearly to the level of the junction of either platinum wire with the plate, was made part of the circuit of a galvanometer and a Daniell cell by means of a key; its poles were connected with the electrometer, and before pressing down the key which put the cell into the galvanometer circuit, it was made insensitive by an impulse. On pressing down the key, the needle of the galvanometer was deflected, and this could not have happened if either contact were broken. In fact, the indication of the galvanometer was the same whether the cell was in the sensitive or in the insensitive state.

In two or three cells in which the alcohol had partially evaporated, leaving a portion of the sensitive plate above the liquid, it was found that, the whole plate having been originally positive, the portion in the vapour gave a negative E.M.F., while the lower portion continued positive.

Among the numerous liquids tried in these cells was butyric acid, which is efficacious; but after a few days it acts on the tin plate and tends to destroy the sensitive surface. A plate which had been kept in a cell containing butyric acid for some days was removed into one containing propylic alcohol. The effect was that the upper portion of the plate exhibited impulsion-effects—being alternately positive and negative with impulses—while the lower portion remained positive.

In acetone, nitrate of amyl, and glycerine these plates are also sensitive—as indeed in water also; but the E.M.F. in these liquids is less than in methyl alcohol.

It was found also that if the cell contained only the vapour of alcohol, an E.M.F. was generated by light, but less than that in the liquid. In aldehyde no E.M.F. due to light was observed.

Hydroxyl has the effect, after about twenty-four hours, of giving to the plate a yellowish colour, and also of changing the sign of the E.M.F. which exists in the dark.

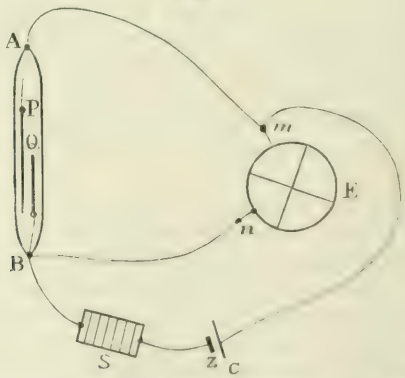
It has been found many times that one effect of removing a sensitive plate from an alcohol cell to a cell filled with hydroxyl or other liquids and then replacing it in the alcohol, was to develop impulsion results; and this fact shows that these results cannot be due to any induced electrification on the glass of the cell and an action of light on this electrification —such an action as has been the subject of recent experiment by a Russian physicist.

If, then, I am right in supposing that the development of electrical charges on these sensitive plates is in some way connected with molecular disturbances produced by electromagnetic induction or mechanical vibration, it must be admitted that the result is possibly a very important one, and that it may play a large part in the economy of nature. Thus, the mode in which solar energy is taken up in the cells of plants may be largely dependent on such disturbances in the atmosphere or in the earth. And in this connexion a somewhat wild conjecture may be pardoned.

The microradiometer of Prof. Boys works wonders in the measurement of very minute changes of temperature. If, then, we imagine a beam of light to be incident on the sensitized plate of an impulsion-cell from which it is, in part, reflected to a microradiometer, when the cell is in its insensitive state the incident energy is not taken up electrically and statically, and a greater portion of it would be sent to the radiometer than would be sent if the cell were in the sensitive state, so that a mechanical tap or an electromagnetic impulse, in altering the cell from electrical insensitiveness to sensitiveness, should produce an effect on the radiometer.

Connexion with the Daniell Cell.—It has been already stated that the residual effect when light is withdrawn from the cell is got rid of by connecting the cell with a Daniell cell in such a way that the deflexion caused by the latter is opposed to that produced by light—*i. e.*, the sensitive plate, P (fig. 4), is connected with the copper pole of the Daniell.

Fig. 4.



A very curious result of this arrangement deserves to be mentioned, inasmuch as it may possibly afford a clue to the nature of the action of light on the sensitive plate. Between the Zn pole of the Daniell and the plate Q interpose a very

great resistance, S, of the same order of magnitude as the resistance, R, of the photoelectric cell itself—*i. e.*, several megohms. This resistance S is composed of lead lines traced carefully on glass and then covered with shellac, and is, in my experiments, something like 10 megohms. The poles, A, B, of the cell being connected with the electrometer, if e is the (disturbing) E.M.F. of the cell in the dark (which may be zero or very small), and E that of the Daniell, we shall obtain a deflexion, Δ, given by the expression

$$\Delta = \pm e + \frac{R}{R+S}(E \mp e),$$

the signs $\pm$ being taken according as e produces a deflexion in the same sense as E or in the opposite sense. This is on the assumption that e is not modified by E, which is possibly false, but not material to the result. Whether e is or is not modified by E, it is clear that if S is very small compared with R, the deflexion on the scale will simply indicate E, no matter how great e may be; and hence if light is allowed to fall on the cell with this arrangement, *there will be no indication of its effect on the scale.* But taking S of the same order of magnitude as R, we obtain, when the cell is in the dark, a deflexion of, say, half the amount produced by the Daniell alone. When the connexions are those indicated in fig. 4, *i. e.* when the Cu pole is connected with the sensitive plate, if light is allowed to fall on the cell a very large deflexion of the spot (of course in the direction opposed to Δ) is produced. If after this we reverse the connexions, *i. e.* connect the Zn pole with the sensitive plate, and allow the spot to settle to its position of rest in the dark, and then let the light fall on the cell, the deflexion produced by light is *very much smaller than before.* To quote a particular case—when the Cu pole was connected with the sensitive plate and the spot came to rest, the spot was deflected from this point through 260 divisions on the scale; and when the connexions were reversed and the spot again allowed to come to rest, it was deflected from the point of rest through only 50 divisions.

From the above expression it is obvious that, in the first mode of connexion with the Daniell, the deflexion from the zero produced by light is $e-\lambda+\frac{R}{R+S}(E-e+\lambda)$, where λ is the E.M.F. due to light, on the supposition that R is constant, so that the observed deflexion on the scale from the point of rest due to the Daniell is

$$\lambda\left(1-\frac{R}{R+S}\right), \text{ or } \frac{S}{R+S}\lambda;$$

and if λ were the same in the second mode of connexion, the deflexion would be also of this value ; but since the deflexion is very notably less in the second case, it is almost certain that λ is also less.

Observe that in the first mode of connexion the action, or possibly only the tendency, of the Daniell is to deposit a layer of oxygen on the sensitive plate ; and if light tends to reduce oxygen at the surface, its action would be increased owing to the additional layer due to the Daniell ; while with the reverse connexions, the reducing action of light would obviously be lessened.

The electrolytic action of a Daniell battery on one of these cells is not permanent ; it disappears rapidly, and, indeed, it is not certain that anything more than a strain tending to electrolysis is produced.

The current of a Daniell cell, or any battery, if passed through an impulsion-cell, does not influence the state of the cell—*i. e.*, this current does not alter the sensitive to the insensitive state, or *vice versâ*.

Supposing S, and therefore Δ, to be such that when (in the first case) light falls on the cell, the spot on the scale is brought back just to the zero from which it started, if the Daniell is suddenly removed the light will then cause a further deflexion—which is the normal amount due to the light. This fact agrees perfectly with the theory of a reducing action, because, in the position of equilibrium of the spot when both light and the opposing Daniell act, the rate at which light tends to reduce is equal to that at which the Daniell tends to deposit oxygen ; and therefore in this particular case the plate is really in its normal state, so that when the Daniell is removed, light finds the plate in the condition in which it would be if no Daniell cell were connected with the photoelectric cell.

Action of Different Colours.—In a sensitive tin-foil cell, the action of the blue part of the spectrum is very much greater than that of any other part ; but measurable results can be obtained all through, as will be seen by the diagram exhibited to the Society. The spectrum was that of lime-light passed through a prism of bisulphide of carbon, a single cell being used in the experiment. This cell has been, from time to time, under experiment for more than four years, and its action is now exhibited to the Society. It has not appreciably deteriorated, but the time of any one exposure has never been more than a few minutes.

Seleno-Aluminium Cells.

In the year 1880 Mr. A. Graham Bell utilized the property of conductivity possessed by a modification of selenium which had been previously found to be a conductor, and also the property of variable conductivity when light of variable intensity falls upon it. These properties, as is well known, were utilized in the reproduction of sound by means of a telephone and a battery in the external circuit of which was placed a sensitive selenium conductor. This selenium arrangement is usually called a "selenium cell," but a *selenium conductor* or a *selenium resistance* is a much more appropriate term.

When the photophone was announced, selenium resistances were made in this country first, I believe, by Mr. Shelford Bidwell, who showed some of them at the last meeting of this Society, and by means of them produced two results of striking beauty, which I shall presently endeavour to reproduce by different means.

Last year I set about constructing selenium cells, properly so called—that is, cells in which electromotive force is produced by the action of light. The method adopted was to take two small clean plates of any metal, to spread a thin layer of the already recognized sensitive selenium on the surface of one of them, and, connecting each with a fine platinum wire, to immerse them in presence of each other in a small glass cell containing a liquid. Thus a large number of metals and a large number of liquids had to be tried for the best result. Plates of platinum, silver, tin, copper, zinc, bismuth, mica, glass, and other substances were tried with various liquids. With copper the E.M.F. produced by light was almost, if not quite, zero. All the others gave considerable results; but much the best result was obtained with plates of aluminium; and for some time the liquid used was one of the alcohols—preferably methylic. In the course of a few days, however, the aluminium plates in alcohol were found to be covered with a kind of gelatinous deposit, which, I am told, is an aluminate of alcohol. This liquid was, therefore, abandoned; and the best result of all was found to be produced with *acetone*.

The process of forming the sensitive plate is as follows:—On an iron tripod is supported a porcelain plate which is heated from below by a Bunsen flame; the little strip of cleaned aluminium is placed on this plate, and when it has got hot, one end of it is held in a forceps, while a drop of melted selenium placed at the end of a very hot glass rod is

rapidly smeared over the aluminium plate. This selenium layer should be of uniform thickness, and the thickness must be neither very great nor very small. When the layer is deposited, the aluminium plate is quickly removed from the porcelain plate by the forceps and rapidly moved up and down in the air for a few seconds, the gas-flame being, at the same time, removed from under the porcelain plate. Both plates having now become slightly cooler, the aluminium plate is replaced on a comparatively cool part of the porcelain plate, and any tendency of the selenium to become liquid is checked by blowing over its surface. Working the gas-flame now rapidly backwards and forwards under the porcelain plate and occasionally blowing over the selenium surface, a series of changes—very much resembling those presented in the preparation of a sensitive tin surface—are observed. The appearances are as follows :—

1. The originally jet-black selenium surface gradually assumes a bluish-white appearance.

2. As the process is continued, this latter surface becomes a grey which may be of several shades. It may be a light grey, or a grey with a violet tinge, or a grey with some glossy spots or streaks. None of these surfaces is to be accepted. They are the final forms which most readily present themselves ; and when they do, the selenium must be melted afresh and again spread over the aluminium plate—the whole process being repeated with its gradual heatings and coolings, until finally—

3. The surface of the selenium assumes a very dark brown colour.

This is the most sensitive surface that can be obtained. At first, accepting too literally the statement that "the grey modification of selenium is the sensitive one," I accepted every plate which finally assumed a grey appearance, and constructed a large number of cells for a battery. By accident, however, a plate with the brownish colour was formed, and it proved to be so much superior to the others, that they were all rejected.

The glossy spots and streaks which sometimes exist on the grey surfaces are, I think, due to an indefinitely thin layer of the black selenium which has escaped the necessary transformation ; and to observe them, it is well to look at the plate almost in the plane of its surface. The dark brown surface is devoid of them, and is in appearance quite homogeneous.

When the plate has assumed this appearance, it may be screened from light and left on the porcelain plate to get

cool, for which about ten minutes will suffice. When the plate has cooled, it can, apparently, be kept in the dark, unimmersed in any liquid, for any length of time before being put into the acetone cell. A plate was thus kept for sixteen days, and then, on being placed in the acetone cell, it was as sensitive as if it had been immersed immediately after formation. It is a marked peculiarity of the seleno-aluminium cell that, immediately after it has been set up, it is wonderfully rapid in its response to light, and that on the withdrawal of the light the E.M.F. at once disappears; but after a few days it is much slower in both respects—particularly the latter—while its sensitiveness as regards the magnitude of the E.M.F. developed is unimpaired.

The dispersion of the residual effect is produced by the means before described for the tin cells, viz., connexion with a Daniell cell, the sensitive plate being now, of course, connected with the Zn pole of the Daniell.

No sensitive and insensitive states due to vibrations, mechanical or electromagnetic, have, so far, been observed in the seleno-aluminium cells.

Sign of the E.M.F. due to Light.—Unlike the tin-foil plates described, the sensitive plate in a seleno-aluminium cell is strongly *negative* towards the insensitive plate when the cell is exposed to light.

Effects of Different Colours.—The seleno-aluminium cells differ from all other photoelectric cells that I have constructed in their great sensitiveness to all parts of the spectrum, the maximum effect being produced in the yellow near the borders of the green.

No very accurate experiment has yet been made on this subject, because the Thomson quadrant-electrometer at my disposal happens to be out of order; but with Clifton's form of the instrument, in which great sensitiveness has been aimed at rather than accuracy or constancy, the following numbers represent the relative electromotive forces produced by the spectrum of an albocarbon light formed by a bisulphide-of-carbon prism :—

Red	109
Border of red and yellow . .	117
Yellow	130
First edge of green	113
Last edge of green	101
Middle of blue	104
End of blue	102

The E.M.F. of a Daniell was represented by 408, and the

cell was about one metre from the prism. Most probably, of course, the number 101, corresponding to the border of green and blue, is less than it should be.

All other photoelectric cells may almost be said to be sensitive to the blue alone.

Effect of Continuous Exposure to Light.—The effect of exposing a seleno-aluminium cell continuously to daylight depends on whether the cell is left on open or on closed circuit. A cell left on open circuit for many hours, and then kept in the dark until its E.M.F. settles down, will be found to have fallen to one fifth of its original value; but if then kept during the night and observed in the morning, the E.M.F. produced by exposure to light will have quite recovered its first magnitude. Not so with the cell on closed circuit; its E.M.F., on fresh exposure, will be reduced to nearly one half its original value.

A cell which had been exposed to daylight for five days (with, of course, the advantage of each night's resuscitation) is now shown to the Society, and its action can be compared with that of a fresh cell.

Connexion with a Daniell during Exposure.—When a Daniell with a very great resistance interposed, as described in connexion with the tin cells, is connected with a seleno-aluminium cell, so that the Zn pole is first connected with the sensitive plate, and then with the insensitive, the E.M.F. developed by light is much greater in the first case than in the second—a result which is the same as before, since the seleno-aluminium plate is the negative one in the cell, and therefore the effect of this connexion with the Daniell is to develop between the poles of the photo cell a difference of potential opposed in sign to that which light produces.

Mechanical Effects.—The E.M.F. generated by light in a photoelectric battery can be utilized for ringing electric bells, lighting or extinguishing electric lamps, and possibly other things, although the materials of the battery are never used up in producing currents. The method which I have employed consists in utilizing the motions of an electrometer needle (due to the E.M.F. of the photoelectric battery) for making a contact and completing the circuit of an ordinary voltaic battery, whose current, thus completed, rings a bell, lights a lamp, &c.

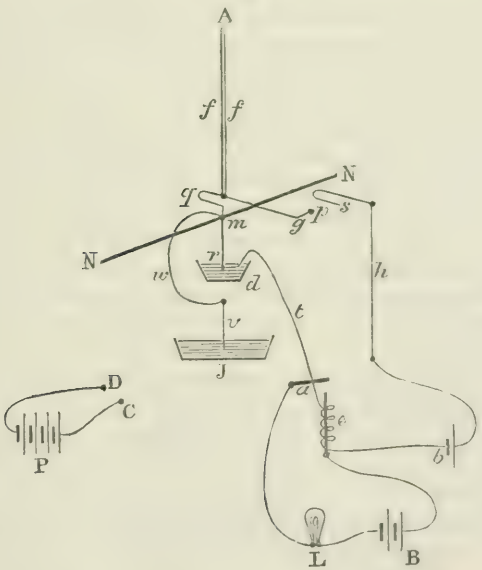
The first arrangement which I employed for this purpose was as follows:—At the middle of the aluminium needle of a quadrant-electrometer, and at right angles to the length of the needle, is fixed a very fine glass tube about $1\frac{1}{4}$ inch long; a platinum wire traverses the interior of this glass

tube and, coming out at its ends, this wire terminates in two little spheres of platinum. Over the quadrants were fixed two small mercury-cups which were completely insulated from the quadrants and which were permanently connected with the poles of an external battery which had an electric bell in its circuit. When light shone on the photoelectric battery (whose poles were connected with those of the electrometer), the needle was deflected and, carrying the little glass tube with it, brought the platinum points into contact with the mercury in the cups; thus the circuit of the voltaic battery was completed, and the bell rung. This arrangement was unsatisfactory, owing to the difficulty with which the platinum points separated from the mercury, and it has been replaced by a much more satisfactory plan devised by Mr. Appleyard, to whom I beg to express my thanks for the untiring perseverance which he devoted to the perfecting of the apparatus.

The improved arrangement is as follows :—

In the figure N N represents the needle of the quadrant-electrometer, the quadrants of which are not represented;

Fig. 5.



$g\,q\,m$ is a very fine glass tube passing down through the middle point, m, of the needle; a platinum wire, $p\,g\,q\,m\,r$, traverses this tube, the portion $g\,q$ lying at right angles to

the long diameter, N N, of the needle, and terminating in a sphere, p ; the portion $m\,r$ of the wire dips into a shallow dish, d, of mercury which is supported below the quadrants by an arm not represented ; a platinum wire, t, dips into the dish d, and, passing outside the case of the electrometer, is connected with one end of the coil of a small electromagnet, e, whose armature is a ; the other end of this coil is connected with one pole of a weak voltaic cell, b, whose other pole is connected with a small platinum plate, s, through a support, h, which is fixed inside the case of the electrometer, and, of course, insulated from the needle and the quadrants ; the platinum plate s is fixed tolerably close to the position of rest of the platinum point p ; and when the needle is deflected by the E.M.F. of a photoelectric battery, P, connected with the poles, C, D, of the electrometer, the point p comes into contact with the plate s and completes the circuit of the voltaic cell b, and thus brings the armature a into contact with the magnet of the coil e : this connexion completes the circuit of a voltaic battery, B, in whose circuit is an incandescent lamp, L, or an electric bell, which is then set in action. The needle is connected with the sulphuric acid jar, J, by means of a fine platinum wire, w, bent into a semicircular form so as to avoid contact with the dish d when the needle moves, the wire w terminating in a vertical length exactly under the centre of the needle ; thus, since the wires r and w are in the vertical axis of rotation of the needle, no appreciable friction hinders the motion of the needle.

The needle is suspended by two fine silk fibres, f, f, from a support A inside the case of the electrometer. Instead of the *two* external voltaic batteries, B, b, *one* would theoretically suffice ; but it is found that, to prevent sparking and "stiction" between p and s when the current is made, it is preferable to have a very weak current traversing this portion of the arrangement—one which is just sufficient to work the electromagnet e.

In this way, by means of a few seleno-aluminium cells, P, I have found no difficulty in ringing a bell by the light of a taper or that of a match held at a distance of a few feet from the battery P. Observe that by this method we never draw on the materials of the photo-battery, because no current ever passes through it ; it is simply connected with the poles of the electrometer, and its E.M.F. alone is employed.

The Problems of Photoelectricity.

Three prominent problems in this subject deserve to be signalized. The first, and least pretentious, is the construc-

tion of a really scientific photometer. It cannot be said that the comparison of two lights by means of a spot of grease is a very satisfactory procedure ; but in the seleno-aluminium cell we have, on account of its great sensitiveness and range in the spectrum, an approximation to the possibility of an electrophotometer—at least so far as the *comparison* of lights is concerned. For, assuming that, by means of such a cell, we take, as it were, each light to pieces, and note the intensities of the different colours—which are directly proportional to the squares of the corresponding electromotive forces—we could then apply the principle of Newton's chromatic circle to determine the value of the resultant light. The second problem—and that which in 1877 induced me to work at this subject—is the electrical transmission of an image to any distance ; in other words, the construction of a telephotograph. The problem seems to be one of exceedingly great difficulty—much more difficult than the problem of the telephone—because the parts of an image are *simultaneous* and not, like the sounds of the voice, *successive* ; and, indeed, we have also to deal with a quick succession if we are to transmit a living moving image, such as Homer depicted on the shield of Achilles. The early attempt which I made consisted in the construction of a cable, somewhat on the model of the optic nerve. The optic nerve consists of a bundle of fibres, each a conductor of electricity and each separated from its neighbour by being surrounded by a medium. One set of ends of this nerve abuts on the retina, which is its sensitized plate, and the other in the brain. It is well known that light incident on the eye causes a photographic decomposition on the retina ; and I believe that images have been seen on the retina of a rabbit which was immediately killed after a strong light had been presented to its eye. The images, then, of external objects are transmitted along the optic-nerve cable to the brain, where by some means or other they result in a process of thought. Possibly thought is an equivalent of at least a part of the originally incident energy. No satisfactory solution of this problem will be attained by any slow and painful mechanical process of tracing out in succession the various portions of a picture ; and it does not now seem that we are near any true solution of the problem, whatever startling stories the newspapers may from time to time report.

The third problem is the direct transformation of the radiant energy of the sun into work useful to us, without the consumption (at least on any large scale) of materials on the earth—in other words to get rid of that terrible waster of

energy, the steam-engine. I usually find two objections made against any investigation in this direction. The first is, that the attempt is contrary to the principle of the conservation of energy. The objection, however, does not seem to be well founded; because it is conceivable that a photoelectric battery may yet be found which will simply act as a transformer of the energy which it receives from the sun, while its own materials, being merely the implements used in the process, may be almost wholly unmodified. The energy thus taken out of the sun may finally be radiated out into space from the earth in the form of heat, if it is true that all forms of energy must ultimately pass into this form —a proposition which, being a very wide generalization from our experience on the earth, it may be permitted to doubt in the universal necessity claimed for it.

The second objection is that there is not energy enough in the solar rays at the distance of the earth to supply the work desired. This objection is founded on the experiments of Pouillet, Violle, and others, who have estimated the solar energy incident per square foot per second on the surface of the earth. Let us see how much energy, according to the assumptions based on these experiments, is at our disposal.

The quantity of solar energy, assumed to be measured in metric thermal units, which is incident, normally, every minute on a square centimetre at the distance of the earth is is given by the expression

$$A\, a^{\epsilon},$$

where, according to Pouillet, A (the solar constant) is 1·7633 calories, a (the atmospheric constant) is something between ·7244 and ·7888—let us say that $a = ·75$; and ϵ is the ratio of the thickness of atmosphere traversed to the normal thickness of the atmosphere measured from the place of observation. M. Violle employs a formula of this form, but, according to him, ϵ involves the height of the barometer and the pressure of aqueous vapour present in the air, and $A = 2·54$ calories. At the superior limit of the atmosphere ϵ is, of course, zero, and at the surface of the earth, for normal rays, $\epsilon = 1$. Taking this latter value of ϵ, and converting the thermal units into ergs, the quantity of energy incident per square centimetre per minute is

$$1·3224 \times 42 \times 10^6 \text{ ergs}$$

according to Pouillet, and

$$1·905 \times 42 \times 10^6 \text{ ergs}$$

according to Violle. Converting these into foot-pounds' weight per square foot per second, we have

63·42 foot-pounds' weight per sq. foot per second (Pouillet),
91·35 „ „ „ „ (Violle).

The quantity of solar energy existing at any instant in one cubic foot of space at the surface of the earth is, of course, obtained by dividing these numbers by the velocity of the radiations in feet per second (roughly 10^9), and this quantity is infinitesimally small. Perhaps it is the infinitesimal value of the energy in a cubic foot which impresses people so strongly with the insufficiency of the solar radiation for doing work; but it is obvious that with this quantity we are not concerned. It is the amount which is contained at any instant in the immensely long column through which the energy travels in a second that is important.

The number assumed by Clerk Maxwell ('Electricity and Magnetism,' vol. ii. p. 402) is 83·4, which is very nearly what Pouillet's becomes at the superior limit of the atmosphere.

Thus we see that the amount of power at our disposal is small—yet, perhaps, not hopelessly small.

But is it necessary to accept this deduction from Pouillet's experiments at all? I think not, because it is not by any means certain that a blackened surface, such as that in Pouillet's pyrheliometer, catches up and transforms into heat every form of energy in the solar beam. There may be forms of energy which take no notice of blackened surfaces and which refuse to be converted into heat by means of them. Perhaps the proper receptive surfaces for them remain to be discovered; and it is this consideration chiefly which gives hope to the experimenter in Photoelectricity. The dissipation of every form of energy in the Universe into the final form of heat of uniform temperature is a dogma and nothing else—and, moreover, a dogma which leads to the most dismal results. Can its advocates trace the process in the case of energy incident on the retina, telephotographically transmitted to the brain, and converted into—or, at any rate, productive of—thought; and can they show that after this process nothing but heat remains?

It is not to the purpose to say that, "so far as we know," all forms of energy must run into heat finally, and be diffused throughout the Universe, because we may even still imagine that there are many very astonishing physical facts beyond what we know. Indeed, even in the unspeakably dismal event of the final conversion of the whole "visible" Universe

(whatever that may mean) into one huge dark inert mass of uniform temperature in which no life is possible, this much, at least, is included in what we *do* know—viz., that we shall not have then got rid of the static energy of gravitation ; and I strongly suspect that if we journeyed out to Antares or to Aldebaran, we should meet with intelligent beings who would express the utmost astonishment that we could ever have framed a principle leading to such a universal catastrophe.

XXVI. *On Gold-coloured Allotropic Silver.*—Part I. *By* M. Carey Lea *.

[Plates I.–III.]

THE object of the present paper (which may be considered as a continuation of that published in the American Journal of Science for June 1889) will be:—

1st. To describe the reactions of gold-coloured allotropic silver.

2nd. To show that there exists a well-characterized form of silver intermediate between the allotropic silver previously described and ordinary silver, differing in a marked way from both.

3rd. To prove that all the forms of energy act upon allotropic silver, converting it either into ordinary silver or into the intermediate form. Mechanical force (shearing stress) and high-tension electricity convert it directly into ordinary silver. Heat and chemical action convert it first into the intermediate form, then into ordinary silver. The action of light is to produce the intermediate form only, and even the most prolonged action at ordinary temperatures does not carry it beyond this.

4th. To show that there exists a remarkable parallelism between the action of these forms of force on allotropic silver and their action on the silver haloids, indicating that it is not improbable that in these haloids silver may exist in the allotropic condition.

Reactions.

The most characteristic reactions of gold-coloured allotropic silver are those with the strong acids. When normal silver reduced with milk sugar and alkaline hydroxide is left in contact with strong hydrochloric acid even for several hours, there is no

* From an advance proof communicated by the Author, to whom we are also indebted for the beautiful Plates illustrative of the paper.—W. F.

action, and the silver after thorough washing dissolves in warm dilute nitric acid without residue. With allotropic silver similarly treated, chloride is always formed. But strong hydrochloric acid instantly converts allotropic to ordinary silver, and consequently only a trace of chloride is produced. By largely diluting the acid the conversion is retarded and the proportion of chloride is greatly increased. Thus, for example, when ordinary hydrochloric acid is diluted with fifty times its volume of water and is made to act on allotropic silver, about one third of the latter is converted to chloride. Probably the whole would be but for the simultaneous conversion to normal silver. This double action is very curious, and strongly differentiates allotropic from ordinary silver. Even with the same acid diluted with a hundred times its volume of water, there is a gradual but complete conversion to white silver accompanied by the production of a not inconsiderable quantity of silver chloride.

Neutral chlorides also act strongly upon allotropic silver, even when much diluted. So sensitive is this form of silver to the action of chlorides that if in washing it on the filter river-water containing a mere trace of chlorides is by an oversight used instead of distilled water, a grey film of normal silver will form on the surface.

The reactions above described were obtained with the moist precipitate freshly prepared. By standing for some time, even if kept moist, it appears to undergo a change. When freshly prepared, it is slightly soluble in acetic acid, but after standing for a week or two ceases to be so.

Sulphuric acid diluted with fifty times its volume of water has no action upon normal silver. When made to act upon allotropic silver, it instantly converts it to normal but at the same time dissolves a little of it.

It is rather curious that the dry film of gold-coloured allotropic silver seems to be more easily acted upon by some reagents than the moist precipitate. I have noticed, for example, that oxalic, citric, and tartaric acids do not convert the moist precipitate to normal silver, but films on pure paper are gradually whitened by these acids. It is not a question of strength of solution, for the moist precipitate remained unchanged for twenty-four hours under the same solution which whitened the same material as a dry film.

Ammonia seems to be without converting action, but dissolves a trace. It will be shown in a future paper that there exists a form of allotropic silver abundantly soluble in ammonia.

In those reactions in which allotropic silver acts the part

of a reducing agent, as for example with potassium ferricyanide and permanganate and with ferric chloride &c., its behaviour differs from that of ordinary silver chiefly in showing greater activity. The difference is rather of degree than of kind. The formation by these reagents of coloured films will be described at the end of this paper.

Intermediate Form.

Allotropic silver presents itself in an almost endless variety of forms and colours—gold-coloured, copper-coloured, blue, and bluish green (these last in thin films), red or purple. Most of these varieties seem to be capable of existing in two conditions, of which one is more active than the other.

If we coat a chemically clean glass plate with a film of gold-coloured allotropic silver, let it dry (first in the air, then for an hour or two in a stove at 100° C.), and then heat the middle of the plate carefully over a spirit-lamp, we shall obtain with sufficient heat a circle of whitish grey with a bright, lustrous, golden-yellow ring round it, somewhat lighter and brighter than the portion of the plate that has not been changed by heat. This ring consists of what I propose to call the "intermediate form."

Its properties are better seen by using a film formed on pure paper, one end of which is heated over a spirit-lamp to a temperature just below that at which paper scorches. The change is sudden, and passes over the heated portion of the surface like a flash.

Examining the changed part, we find:—

1st. That it has changed from a deep gold to a bright yellow-gold colour.

2nd. When subjected to a shearing stress it *does not whiten or change colour in the slightest degree.*

3rd. It is much harder, as is readily perceived in burnishing it.

4th. It no longer shows the colour reaction with potassium ferricyanide and ferric chloride, changing only by a slight deepening of colour.

Of these characteristic changes the second is the most remarkable. The gold-coloured silver in its original condition changes with singular facility to white silver: almost any touch, any friction, effects the conversion. If the paper on which a film is spread is creased, the crease is found to be grey. Exposure to heat or to light destroys this capacity for change, and it is often lost by mere standing (even though protected from light) for a few weeks. This evidently indi-

cates some remarkable molecular change. It will be noticed that the anomaly lies in this, that pressure instantly effects the complete change from the original form to normal silver, heat effects the same change but with an intermediate stage, at which stage *pressure no longer produces any action.*

The intermediate form is distinguished from normal silver almost solely by its bright yellow colour and its higher lustre. This last difference is very striking when a film on glass is heated in the manner above described. The central parts, in changing to white silver, become wholly lustreless ; whilst the circle of "intermediate" retains all its original lustre. Its continuity is still complete, so that if viewed through the glass it still acts as a mirror.

This change may be either molecular or depend on dehydration.

The latter seems doubtful, for the change cannot be brought about by desiccation. Films on paper, on glass, and also solid material were kept over sulphuric acid *in vacuo* for twelve days * without bringing about this modification. (They were of course thoroughly protected from light.)

Light is also capable of effecting to some extent this change, as will be described further on.

Copper-coloured Allotropic Silver.

The colour of allotropic silver depends to a remarkable extent on the amount of washing which the freshly prepared material receives.

With a short washing the material dries to a bright yellow-gold colour ; with more washing to a reddish colour ; with still more, the colour is a deep rich copper shade.

The washing, when conducted in the ordinary manner, is exceedingly troublesome ; the material soon begins to run through the filter, and blocks it up.

This trouble may be completely avoided by washing with a 2-per-cent. solution of Rochelle salt instead of pure water, until towards the end of the operation†.

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* A longer time was inadmissible on account of the tendency to spontaneous alteration.

† The mode of preparing the gold- and copper-coloured forms is as follows; the difference is in the length of washing only.

In a precipitating jar are placed :—

Water	800 c.c.
20-per-cent. sol. Rochelle salt	200 ,,
40-per-cent. sol. silver nitrate	50 ,,

Substances of a character nearly related to those that I have described in this and the previous paper, are obtained by acting on silver tartrate with stannous nitrate. The method is more troublesome and gives inferior results, the gold-coloured product is less pure. A beautiful steel-blue substance obtained in this way was found to contain a considerable quantity of tin, probably present as stannic oxide; 10·87 per cent. of tin corresponding to 13·80 SnO_2 was found by analysis. Another analysis gave 10·66 per cent., corresponding to 13·61 SnO_2. In the first case, the quantity of silver found was 83·61, in the second 84·12 per cent. These results do not lead to any satisfactory formula. The tin is no doubt present as an impurity, and as the iron process gave far better results, the examination was not carried further. Silver citrate gives similar results.

Action of Different Forms of Energy on Allotropic Silver.

1. *Action of Electricity.*

High-tension electricity instantly converts gold-coloured silver to the ordinary form. When paper covered with a film of gold-coloured silver is held between the conductors of a Töpler-Holtz machine, each spark forms a grey dot of ordinary silver. A powerful discharge is not necessary; an inch spark from a small machine is effectual, even when the condensers are cut off. There is also a lateral action, which is best seen when several slips of such paper are held loosely together and placed between the conductors. When the slips are opened a little, the lateral branches are beautifully seen, playing through the silver. Their fine emerald-green colour contrasts with the purplish shade of the spark.

When several pieces are in this way held between the conductors together, there is a transfer of silver from one

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In another vessel are placed :—

Water	800 c.c.
20-per-cent. sol. Rochelle salt	200 „
30-per-cent. sol. ferrous sulphate (crystallized)	107 „

(The substances must be added in the order above given, and be mixed immediately before using. It is scarcely necessary to say that distilled water must be used exclusively.) As soon as the mixtures are made the iron solution is to be poured into the silver and vigorously stirred for some time. The white silver tartrate becomes almost immediately bright red, then deepens in colour, and finally becomes black.

piece to the other, so that the back of each piece of paper is blackened by silver carried over from the one behind it.

That the branching grey spots in this way formed are normal silver, is easily proved by immersing the piece in a dilute solution of potassium ferricyanide. The part acted upon by electricity is not affected by the reagent, whilst the rest of the film shows the coloration characteristic of allotropic silver. In Plate I. the upper figure shows a slip of paper, at one end of which electricity has been transmitted; and the figure below, a similar slip that has been subjected to the action of the ferricyanide, showing that where electricity has passed the silver has become normal and is not affected by the reagent.

2. *Action of Heat.*

Allotropic silver is converted by heat to normal silver in either the wet or the dry state.

Dry Heat.—When films of allotropic silver on glass are placed in a water desiccator, and are kept at 100° C. for eight or nine hours, the central portions are converted into the intermediate form, whilst at the edges there is a border of greyish-white ordinary silver. In fact the change to white silver at the edge commences before the central part is fully converted to the intermediate form.

At higher temperatures the change is much more rapid and better marked. At 180° C. the first effect is to darken a little (this is usually the first effect of heat) : this continues about five minutes. Continuing the heat for ten minutes more, the slight darkening disappears and the film has a bright pure gold colour, sometimes with a slight salmon tinge. The change to the intermediate form is now complete, the film burnishes yellow, and does not react with potassium ferricyanide. It is of interest to remark that the colour reaction persists as long as there is a trace of unconverted material, *so that a film may burnish yellow and yet show a well-marked colour reaction.* This is because most, but not all of the material has undergone conversion.

At 200° C. the film begins in about 10 minutes to show a white border, and in half an hour or thereabouts it whitens completely.

Allotropic silver in the solid form heated to 180° or 190° for about 15 minutes undergoes a similar change : whereas before it was easily pulverized, it is now almost impossible to reduce it to powder, and the powder is yellow instead of being greyish black.

Moist Heat.—A film spread on pure paper and placed in distilled water maintained at 99° or 100° without actually boiling, at the end of half an hour is converted almost wholly to the intermediate form. It burnishes pure yellow, but still shows traces of the colour reaction.

A better plan of operating is to immerse a film spread on glass in distilled water, and to place it in a desiccator with a water-jacket. After keeping for twenty-four hours close to 100° C., the film has become pure white. It is not disintegrated by the change, but may be detached from the glass in films exactly resembling ordinary silver leaf.

The effects of heat are shown in Plate I., lower pair of figures.

3. *Action of Mechanical Force (Shearing Stress).*

The slightest application of force suffices to instantly convert gold-coloured allotropic silver to normal silver. A glass rod with a rounded end drawn lightly over the surface of a film on paper, leaves a white trace behind it. The force sufficient to cause this change is so slight, that one might doubt its reality were it not for the decisive proof immediately at hand. First, there is the characteristic change of colour: the film is as yellow and as brilliant as gold leaf; the line drawn by the glass rod is of pure white silver. Immersing the film in a solution of potassium ferricyanide, the white lines simply change to gold colour, whilst the film surface on which they are drawn passes through a brilliant succession of colours. (These effects are represented in Plate II., the uppermost figures.) For this use, freshly made material should be employed, and the film itself should have been freshly spread on pure paper or card and used within a few hours after drying. This because of its easy partial passage, especially in thin films, to the intermediate state, in which it gives a yellow streak. (See also remarks as to partial conversion, *ante*.)

When the experiment is performed under proper conditions, the effect is very striking by reason of the instant conversion of the pure, deep yellow metal to perfect whiteness without a trace of colour.

In an earlier communication to the 'American Journal of Science,' it was mentioned that, having taken with me on a journey several small vials containing gold-coloured silver, they were found at the end of the journey to be all converted into white silver without having undergone any disaggregation, and retaining the original shape of the fragments. The

white silver formed had the fine frosted white colour of pure silver. This change was attributed to the friction of the fragments against each other, occasioned by the motion during the journey; a conclusion that was confirmed by finding that when cotton-wool was forced into the empty part of the vial in such a way as to prevent all internal movement, the substance could be sent over a four-fold distance without alteration.

It was also observed (and this is a matter of special interest) that when a partial change had been effected by friction, this alteration went on, although the substance was left perfectly at rest, until it became complete. With time, all solid specimens of allotropic silver undergo this spontaneous change to bright white silver, apparently normal silver, even when thoroughly protected from light. Out of over twenty specimens in tightly corked tubes, packed in a box and left in a dark closet for a year, not one escaped conversion. Spread on paper or on glass and duly protected, the change is slower.

4. *Action of Strong Acids.*

The action of acids upon allotropic silver has been already described; it remains only to add here that the conversion to normal silver is entirely unaccompanied by the escape of gaseous matter; not a bubble can be detected by the closest observation.

By acting on dry films with dilute sulphuric acid it is easy to make the conversion gradual, and so to trace its passage through the intermediate form.

With sulphuric acid diluted with four times its bulk of water and allowed to cool, an immersion of one or two seconds converts a film on glass or on pure paper wholly to the intermediate form. It is then bright gold yellow, but shows no colour with the ferricyanide reagent.

With sulphuric acid diluted with twice its bulk of water and used whilst still hot, the action is instantaneous, and the allotropic silver is converted into light grey, normal silver. The silver obtained in this way is very indifferent and gives no reaction with potassium ferricyanide, whereas even ordinary silver leaf gives a pale-coloured reaction. (See Plate II., lower pair of figures.)

The same acid after cooling acts more slowly; the product is more yellowish, owing to the presence of a certain quantity of the intermediate form.

5. *Action of Light.*

When allotropic silver is spread as a thin film on glass or on pure paper, it may be preserved for a length of time apparently unchanged. This appearance is deceptive. From the moment that the film is formed, a slow but steady change commences, which can be best explained by supposing that a gradual polymerization takes place. Even after eight or ten hours' exposure to ordinary diffuse light, a distinct loss of activity can be detected by careful testing with potassium ferricyanide. The change which occurs is in the nature of a tendency to a very gradual passage into what I have called the intermediate form, in which the gold-yellow colour remains unchanged whilst the chemical activity is lost or much diminished. Although a commencement of this change can be detected in a few hours, it goes on very slowly. By exposure to one or two days of summer sunshine (a much longer time is required in winter), the change is nearly complete. The exposed portions are lighter and brighter, and in solution of ferricyanide they colour very slowly.

The question naturally arose whether light, by a sufficiently long continued exposure, could complete the change and convert allotropic to ordinary white silver. To obtain a decisive answer the following experiment was made :—

At a window having a south-eastern exposure and unobstructed light, there were placed films on glass and on pure paper. Some of these were placed in a printing-frame under an opaque design ; the others stood side by side with the first, but uncovered. The exposure was continued for four months, from the end of January to the end of May. At the expiration of this time the uncovered paper and glass films were still bright yellow. But of those in the printing-frame the exposed portions had become nearly white, whilst the protected parts retained their full deep gold colour. It may at first seem strange that the uncovered pieces were less affected than those exposed in the frame. But this difference was always observed, namely, that if two films were exposed side by side, the one in a printing-frame under glass, the other simply fastened to a board, the last mentioned was always the less affected. The explanation of this seeming anomaly lies in the fact that allotropic silver is always much more easily affected by heat than by light. The glass in the printing-frame, by exposure to sunlight, becomes hot to the touch, and thus the film under it is kept at a temperature many degrees higher than that of the other film that is freely

exposed to the air; the higher temperature aids the effect of the light *.

It appears, therefore, that the agency of light is somewhat similar to that of the other forms of energy, but very much slower. Experiments made for the purpose demonstrated that it is the more refrangible rays that effect the change.

With light, the production of the intermediate form is never very satisfactory. Long exposures are needed, and before the change to the intermediate form is complete, the further alteration to white seems to commence. With heat the changes are much better marked.

When a film on pure paper has received an exposure of one or two days of summer sunshine under an opaque design, the exposed portions are sufficiently changed to have lost much of their chemical activity, so that when the film is plunged into a bath of potassium ferricyanide, the effect given in the lower figure of Plate III. is obtained; the colour represented is one of an immense variety of tints produced by this reagent on the unaltered or active form. The upper figure of the same Plate gives the effect of a very protracted exposure (as above described) on pure paper (or glass) under glass. With some kinds of sized paper, this effect is produced by a much shorter exposure, apparently owing to the presence of traces of a hyposulphite †, which appears to aid the action of light.

These seem to be not merely new facts, but to belong to a new class of facts. No instance has been hitherto known of an element existing in so great a variety of forms, and passing so readily under the influence of any form of energy from one to another of them.

* Since this was written I find that both Herschel and Hunt noticed an analogous fact in the case of silver chloride, viz. that paper prepared with it darkens more rapidly under glass than when freely exposed; without, however, suggesting the cause, which is the same in both cases. I have observed that silver chloride darkens more rapidly when exposed under warm water than under cold to the same light in vessels side by side.

† The behaviour of these varieties of paper led me to make inquiries of an intelligent paper-manufacturer, from whom I learned that every sort of paper pulp is now treated with chlorine. As any portion of the bleaching material left in the paper would eventually destroy its strength, it becomes necessary to add hyposulphite in excess to remove it. Accordingly every specimen of sized paper that I have examined contained hyposulphite, even the purest photographic papers were not free from it though containing greatly less than most others. Apparently, the only difference is that, with photographic paper more care is taken to avoid any considerable excess of hyposulphite.

It is evident that a connexion must almost certainly exist between these varied transformations and the changes which many silver salts undergo through the action of light and other forces. This connexion will form the subject of the second part of this paper. The present part will be concluded by a somewhat fuller description of the colour reaction which is especially characteristic of allotropic silver.

The Colour Reaction.

When allotropic silver is immersed in a solution of a substance readily parting with oxygen or sulphur, or with a halogen, a film is formed which exhibits the colours of thin plates. Such phenomena are familiar, and are seen in the bluing or yellowing of steel in tempering, and the colouring of other metals when covered with films of oxide or sulphide. With allotropic silver the colours are very brilliant, probably because silver is the best of all reflectors for rays having a nearly perpendicular incidence, sending back about 90 per cent. of such. Light gold-coloured silver gives the most brilliant effects.

The substances which produce these reactions are potassium ferricyanide and permanganate, ferric and mercuric chlorides, alkaline hypochlorites and sulphides, mixtures of potassium bichromate with hydrochloric or hydrobromic acid, solution of iodine, &c.

Potassium ferricyanide in a five or ten per cent. solution is the best of these reagents, because its action is more distinctive. In particular, the blues which it gives are of great purity and the purples very rich. Ferric chloride gives beautiful tints, especially a peculiar glittering rose-colour. It must be very much diluted, until the solution loses its yellow colour and takes a straw shade. It often happens that the characteristic colour does not appear whilst the film is in the solution, but a bronze shade only, the permanent colour appearing only after the film has been dipped into water and blotted off. Potassium permanganate also gives rise to a beautiful succession of colours on allotropic silver, but is somewhat uncertain in its action.

A ferricyanide is therefore the best reagent. As to the substance constituting the film which is formed, it is difficult to say whether it is silver suboxide or ferrocyanide. When potassium ferricyanide is allowed to act on moist allotropic silver suspended in it, and the action of the ferricyanide is carried to its limit, the silver is entirely converted into a

yellowish-white powder, consisting almost wholly of silver ferrocyanide mixed with a little silver ferricyanide.

Of the many varieties of ordinary silver which exist, allotropic silver is convertible into two only. The high-tension spark, heat, and acids convert it to dull grey silver ; on this variety potassium ferricyanide has no action whatever, as will be seen by an inspection of the Plates. Light (under glass) and pressure each convert allotropic to bright white silver, and on this form potassium ferricyanide acts slightly, converting the silver colour to gold. It is needless to say that this gold colour has nothing to do with allotropic silver ; it seems to be produced in the following way :—

When potassium ferricyanide acts on films of allotropic silver, its first effect is to deepen the gold colour to a gold brown, passing rapidly on to other shades. The action on the bright white silver is very slight and apparently just reaches this gold stage, which corresponds to an air-film having a thickness of from 0·000150 mm. to 0·000160 mm.

The succession of colours obtained on allotropic silver with potassium ferricyanide is as follows :—

First Order.

Russet-brown.
Brown-red.

Second Order.

Rich and deep purple.
Dark blue.
Bright blue.
Pale blue.
Green russet.
Red.

Third Order.

Reddish purple.
Bluish purple.
Rich green.

The fourth order is not reached, for after this the colours become much mixed, probably the action is no longer sufficiently uniform. The other differences, besides the absence of the fourth order, as will have been observed, are that, in place of the yellow of the second order corresponding to a thickness of air of 0·000432 mm., there is a green though of a more russet shade than that of the third order.

In the third order there is at no time a pure blue corresponding to 0·000602, but only a succession of beautiful red and blue purples, gradually passing into green.

There are few more beautiful experiments than to watch these changes. Purity of colour, however, depends much on the purity of the paper employed. Want of this purity will often cut short the changes at the pale blue of the second order.

I have endeavoured to give some idea of these colours in the Plates which accompany this paper, but it has proved to be a most difficult task. The colours represented are—

Plate I., purple and blue of the second order.

Plate II., purple of the second order and green of the third order.

Plate III., brown-red of the first order.

It has not, however, been found possible to correctly reproduce the brilliancy and depth of colour of the originals.

Explanation of the Plates.

In each pair of figures the upper one represents the effect of exposing allotropic silver to some form of energy. The changes are in all cases the same ; the gold-coloured silver is converted by all forms of energy to ordinary silver.

In the lower of each pair of figures the effect is represented which would be produced by immersing the upper one in a solution of potassium ferricyanide. This affords proof of the completeness of the change by showing that gold-coloured silver in passing into the ordinary form has lost its power of reacting with a ferricyanide. In these lower figures an attempt has been made to show some of the colours produced in this way. But they fall short of the originals in brilliancy and intensity. These last are so remarkable that the lithographer who executed the work remarked that even an artist with a brush and palette of colours could not imitate them, and that, therefore, it was hopeless to expect to reproduce them by lithography. In other respects the Plates represent fairly well the changes that take place.

Philadelphia, Jan. 24, 1891.

XXVII. *Some Experiments with Selenium Cells.* By Shelford Bidwell, *M.A., F.R.S.**

IT is well known that selenium, like sulphur, which it closely resembles in its chemical properties, is capable of existing in several distinct forms, differing greatly in appearance. The modifications most commonly met with are

* Communicated by the Physical Society : read December 12, 1890.

known as the black amorphous or vitreous, the red amorphous, and the crystalline forms. Selenium is, I believe, always supplied commercially in the vitreous condition. Vitreous selenium is as structureless as glass, and, when its surface is smooth and clean, it is very like black sealing-wax in appearance. In thin films, however, it is seen to be transparent and of a ruby-red colour. It melts, after first softening, at a temperature of about 100° C. Red amorphous selenium is a finely divided brick-red powder, which, at a temperature of from 80° to 100°, becomes transformed into the ordinary dark-coloured vitreous form. Crystalline selenium is obtained by keeping melted vitreous selenium at a temperature of from 100° to 200° for some time, the black liquid mass being gradually converted into a hard slate-coloured solid. This form of selenium melts at 217°: it resembles a metal in appearance, and even in the thinnest films it is quite opaque to light.

In the vitreous condition selenium is a practically perfect non-conductor of electricity: so it is also in the powdery condition if perfectly dry. Crystalline selenium, on the other hand, is, according to the books, a good conductor. In comparison with true metals, however, it conducts rather badly. I found some time ago that the specific resistance of a plate of crystalline selenium, which had been annealed for several hours in a glass mould, out of contact with any metal, was 2500 megohms, while that of another specimen annealed in contact with copper electrodes was 0·9 megohm, the lower resistance in the latter case being due, as I then suggested and still think probable, to the formation of copper selenide during the heating.

A very remarkable fact, first published by Mr. Willoughby Smith in 1873, is that the resistance of crystalline selenium appears to be temporarily diminished by the action of light. This effect is easily shown by means of a small piece of crystalline selenium fitted with wire electrodes and joined up in circuit with a battery and a reflecting-galvanometer. The galvanometer-deflexion is increased when the selenium is illuminated.

In order that the resistance of a so-called "selenium cell" may be kept as low as possible, and the light made to produce a maximum effect, three conditions have to be aimed at. The electrodes should be large; they should be near together; and the selenium, in order to expose a large surface relatively to its volume, should consist of a thin film. Several contrivances have been proposed with the view of fulfilling these requirements. A simple and, I believe,

effective one is that which I suggested ten years ago ('Nature,' vol. xxiii. p. 58). A fine copper wire is wound upon an oblong strip of mica from end to end, the number of turns being about 20 to the inch: a second wire is then wound on, parallel to the first, the turns of the second wire alternating with those of the first; great care is taken that the two wires do not touch each other anywhere. A thin layer of melted selenium is spread over one surface of the mica, filling the spaces between the wires. The film is first quickly cooled by placing the mica upon any convenient cold surface, then it is crystallized by heating at a temperature of about 200°, and, lastly, it is annealed by gradually lowering the temperature for several hours. A cell made in this manner, with a surface of about 10 sq. cm., is generally found to have a resistance in the dark of from 50,000 to 100,000 ohms. As a rule, those cells which have an unusually low resistance are less sensitive to light than others. In a cell of average quality the resistance is reduced about 50 per cent. by the light of an ordinary gas-flame at the distance of one foot.

I made a number of cells on this plan in the years 1880 and 1881. Up to the end of 1882 they were frequently used, and no material falling off in their sensitiveness was noticed. Thirteen of these cells were laid aside until 1885. They had then for the most part deteriorated more or less, one or two of them being quite useless. They were again put away until the present year, 1890, when it was found that only one of the thirteen retained its original sensitiveness and resistance unimpaired.* A second one worked fairly well with a feeble current, its resistance with a single Leclanché cell being in the dark 14,000 ohms, and when illuminated by a gas-flame at 12 inches, 8000 ohms; but with a battery of six cells the resistance became variable and unsteady, as if there were a loose contact somewhere, and a continuous boiling noise was heard in a telephone introduced into the circuit. The resistance of the remaining eleven cells had fallen enormously, in some cases to less than 10 ohms, and they were quite insensitive to the action of light. An attempt was made to restore most of them by melting down the selenium and recrystallizing and annealing; but though the resistance could in this manner be brought up again to a high point, the sensitiveness of the renovated cells was in all cases found to be very poor.

Prof. Adams states (Phil. Trans. vol. clxvii. p. 348) that

* This cell had the unusually high resistance of 400,000 ohms, reduced by the light of a gas-jet at one foot to 190,000 ohms.

in the course of a year the resistance of most of the pieces of selenium with which he performed his well-known experiments fell very considerably, and it would be of great interest to know what is the cause of this curious phenomenon. In the case of my own cells, I satisfied myself that it certainly was not due to any short-circuiting of the wires by contact; and I suggest that it may be owing to the presence of an excessive amount of conducting selenide formed by the union of the selenium with the metal of the electrodes. Each wire is covered with a layer of selenide, which gradually increases in thickness at the expense of the free, badly-conducting selenium, and thus the resistance of the cell slowly falls. At length the layers of selenide become so thick that the coatings upon the two wires actually meet and touch each other. Thereupon the cell is short-circuited; its resistance no longer depends upon the selenium but upon the metallic selenide, which is a good conductor.

I have in a former paper (Proc. Phys. Soc. vol. vii. p. 129; Phil. Mag. Aug. 1885, p. 178) given reasons for believing that the presence of a certain amount of metallic selenide is essential to the sensitiveness of a cell, and I have stated my opinion that the true function of the prolonged heating, generally termed "annealing," is the formation of this necessary selenide, which, when a current passes through the cell, is electrolysed, selenium being deposited upon the anode wire. With the weak currents generally used, the quantity of deposited selenium would be very small, and would at once unite with the metal of the electrode. But if a sufficiently strong current were passed, it is conceivable that the selenium might be separated in quantities too great to be disposed of in this manner. Then the free selenium around the electrode ought to be visible. This view is confirmed by a recent experiment. A cell was made last October with new selenium and the usual copper-wire electrodes. It was well annealed, and its resistance was about 50,000 ohms. The cell was connected to a 26-volt battery, and left for two days. At the end of that time the cell presented a remarkable appearance, those portions of the anode wire where the selenium coating happened to be thin being covered with red feathery tufts, some of which had dropped off and fallen upon the paper on which the cell was lying. Ordinary tests showed that the red stuff consisted, mainly at all events, of red amorphous selenium. But it was clearly moist. All very fine powders seem to attract moisture from the atmosphere; but in the present case the moisture appeared to be greater than could be thus accounted for. An examination

under the microscope disclosed the presence of a number of minute lumps of a white substance, intermixed with the red stuff. The lumps had the appearance of pieces of calcium chloride which had been exposed to the air, and they were clearly the origin of the moisture. They consisted, no doubt, of selenium oxide or hydroxide, which is probably a deliquescent substance.* This oxide might perhaps be formed by the direct combination of some of the freshly separated selenium with the oxygen of the air, or with that resulting from the electrolysis of traces of water existing in the cell.

In the discussion which followed the reading of my former paper, the late Mr. J. W. Clark took exception to a hypothesis therein put forward as to the probable action of the selenides formed in selenium cells, on the ground that selenide of copper conducted metallically and not electrolytically. This he stated to have been experimentally proved by Hittorf (*Pogg. Ann.* vol. lxxxiv. 1857, quoted by J. W. Clark, Proc. Phys. Soc. vol. vii. pp. 119, 120†; Phil. Mag. July 1885, pp. 38, 39). But if the amorphous selenium surrounding the anode in my recent experiment was formed otherwise than by electrolysis, it is difficult to imagine why it should be confined to the anode, as was seen to be the fact, and not extend also to the kathode and other portions of the cell. The inference seems to be that copper selenide does conduct electrolytically‡.

When the resistance of this cell was tested with the Wheatstone's bridge, it was found to have diminished enormously. It was also not sensibly affected by illumination, but, on the other hand, it appeared to be dependent in a curious way on the direction of the current used in testing. With one Leclanché cell and equal proportional coils of 100 ohms each, the resistance with a current from anode§ to kathode was 4500 ohms, and with a current in the opposite direction only 2900 ohms. The change occurred with great regularity as often as the current was reversed.

The cell was then connected directly to the galvanometer without any battery, and a very small polarization current from kathode to anode through the cell was indicated. While thus connected, a piece of magnesium ribbon was burnt near the cell. Instantly the spot of light was deflected off the

* Since the above was written, Prof. S. U. Pickering, F.R.S., has told me that the oxides of selenium are deliquescent.

† This paper of Mr. Clark's, though printed in the 'Proceedings' before my own, was in fact read after it.

‡ The cell with the red amorphous selenium on the anode was exhibited to the meeting.

§ The wire upon which the amorphous selenium was deposited is here and afterwards called the anode.

scale by a current in the opposite direction (*i. e.* from anode to kathode internally), returning to its former position as soon as the magnesium was extinguished. This was not a thermo-electric effect, for the approach of a hot brass rod caused a smaller current *from kathode to anode*, which subsided slowly and not suddenly when the rod was withdrawn.

Photoelectric currents of this character had been previously observed by Prof. Adams and by Mr. Fritts of New York, but no explanation of their origin has been attempted. Perhaps the behaviour of my cell may suggest the direction in which the source of such currents should be looked for, but I have not yet followed up the inquiry.

In the illustration of lectures it is often desirable to be able to exhibit experimental effects in a striking and attractive manner. The movements of a spot of light upon a scale may be convincing, but they are hardly impressive. Yet the resistance of sensitive selenium cells is so high that the variation, under the influence of light, of currents passing through them cannot easily be demonstrated to an audience in any other manner than by their action upon a reflecting-galvanometer. With sufficient battery-power they may, however, be made to work a delicate relay, and thus to produce indirectly a great variety of startling effects. For example, a selenium cell may be connected with a relay and a battery in such a manner that a bell is rung when the cell is in the dark and ceases to ring when the cell is illuminated ; the bell circuit remaining closed when the current through the selenium circuit is below a certain strength, and being broken by the relay when the selenium current is increased by the action of light. It is possible that if selenium cells could be made to retain their sensitiveness for a reasonable time, an arrangement of this kind might receive a practical application. It might be used to give notice of the accidental extinction of railway signal-lamps or of ships' lights ; and if the connexions were so made that light and not darkness set the bell in action, it might be employed for the protection of safes and strong-rooms, the mere light of a burglar's lantern being sufficient to give an alarm.

Again, if the relay is connected with an electric lamp instead of a bell, it constitutes a contrivance by means of which a light is provided automatically when required, and extinguished when no longer wanted. It gives us a lamp which will light itself in the dark and put itself out in the light. The relay can be adjusted so that the lamp may be turned out when the external illumination reaches any desired

point, the diffused light of a dull December day being quite sufficient to act upon the selenium *.

But I do not at present attach any serious importance to such practical applications of these devices. I regard them simply as affording somewhat attractive illustrations of the effect of light upon the resistance of selenium.

XXVIII. *Visibility of Interference-Fringes in the Focus of a Telescope.* *By* Albert A. Michelson.†

WHEN the angle subtended by an object viewed through a telescope is less than that subtended by a light-wave at a distance equal to the diameter of the objective, the form of the object can no longer be inferred from that of the image. Thus, if the object be a disk, a triangle, a point, or a double star, the appearance in the telescope is nearly the same.

If, however, the objective is limited by a rectangular slit, or better by two such, equal and parallel, then, as has been shown in a former paper ‡, the visibility of the interference-fringes is in general a periodic function of the ratio of α, the angular magnitude of the source in the direction perpendicular to the length of the slits, and α_0, the "limit of resolution." The period of this function, and thence $\frac{\alpha}{\alpha_0}$, may be found with great accuracy; so that by annulling the greater portion of the objective the accuracy of measurement of the angular magnitude of a small or distant source may be increased from ten to fifty times. As ordinarily understood, this increase of "accuracy" would be at the cost of "definition" (which in this sense is practically zero); but if by "definition" we mean, not the closeness of the resemblance of the image to the object, but the accuracy with which the form may be inferred, then definition and accuracy are increased in about the same proportion.

In almost every case likely to arise in practice, the form of the source is a circular disk; and if the illumination over its surface were uniform, the only problem to be solved would be the measurement of its diameter. But in many cases the distribution is anything but uniform. If the curve repre-

* Experiments with the bell and the lamp were shown at the meeting.

† Communicated by the Author.

‡ "On the Application of Interference Methods to Astronomical Measurements" (Phil. Mag. July 1890).

senting the distribution along the radius be $i=\psi(r)$, then the element of intensity of a strip $y_1 dx$ will be

$$\int_{-y_1}^{y_1} \psi(r) dy = \phi(x),$$

and it has been shown that the visibility-curve in this case is

$$V = \frac{\int \phi(x) \cos kx}{\int \phi(x) dx}.$$

This may be proved as follows:—

The intensity of the diffraction-figure of a luminous point in a telescope with a symmetrical aperture is *

$$I^2 = \left[\iint \cos \kappa \mu_1 x_1 \cos \kappa \nu_1 y_1 dx_1 dy_1 \right]^2, \quad . \quad . \quad . \quad . \quad (1)$$

in which $\kappa = 2\pi/\lambda$, μ_1 and ν_1 are the angular distances from the centre of the image, and x_1 and y_1 are the coordinates of the element of surface of the aperture.

If μ and ν are counted from the axis of the telescope and x, y, r, are the coordinates of the luminous point, the expression becomes

$$I^2 = \left[\iint \cos \kappa \left(\mu - \frac{x}{r} \right) x_1 \cos \kappa \left(\nu - \frac{y}{r} \right) y_1 dx_1 dy_1 \right]^2. \quad . \quad (2)$$

If now the source is a luminous surface whose elements vibrate independently,

$$\bar{I} = \iint I^2 dx\, dy. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the case of two equal apertures † whose centres are at $x_1 = -\frac{1}{2}a_{11}$ and $x_1 = +\frac{1}{2}a_{11}$,

$$I_{11}^2 = I^2 \cos^2 \tfrac{1}{2} \kappa a_{11} \left(\mu - \frac{x}{r} \right). \quad . \quad . \quad . \quad . \quad (4)$$

This substituted in (3) gives

$$\bar{I} = \iint I^2 \cos^2 \tfrac{1}{2} \kappa a_{11} \left(\mu - \frac{x}{r} \right) dx\, dy.$$

* 'Wave Theory of Light,' Rayleigh.

† More generally, for m equal equidistant apertures whose total area is constant,

$$I_m = I \frac{\sin \frac{1}{2} m \kappa \mu a}{m \sin \frac{1}{2} \kappa \mu a}.$$

Putting $\kappa a_{11}\mu = \vartheta$, $\kappa a_{11}/r = k_{11}$, and expanding,

$$\overline{2I} = \iint I^2 dx\,dy + \cos\vartheta \iint I^2 \cos k_{11} x\,dx\,dy + \sin\vartheta \iint I^2 \sin k_{11} x\,dx\,dy . \quad (5)$$

Let $y = \phi(x)$ be the equation of the curve bounding the luminous surface; or, better, let $\phi(x)dx$ be the "total intensity" of a strip of width dx.

Denoting $\int_{-\chi(x)}^{+\chi(x)} I^2 dy$ by $F(x)$, and omitting the factor 2, equation (5) becomes

$$I = \int F(x)dx + \cos\vartheta \int F(x) \cos kx\,dx + \sin\vartheta \int F(x) \sin kx\,dx,$$

or

$$\overline{I} = P + C\cos\vartheta + S\sin\vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the width of the apertures is small compared with their distance, the variations of $F(x)$ with μ (or ϑ) may be neglected, and in this case the maxima or minima occur when

$$\tan\vartheta = \frac{S}{C}, \text{ or when } I = P \pm \sqrt{C^2 + S^2}.$$

If now the visibility of the interference-fringes be defined as the ratio of the difference between a maximum and an adjacent minimum to their sum

$$V^2 = \frac{C^2 + S^2}{P^2},$$

or

$$V^2 = \frac{[\int F(x) \cos kx\,dx]^2 + [\int F(x) \sin kx\,dx]^2}{[\int F(x)dx]^2} \quad . \quad . \quad . \quad (7)$$

For narrow rectangular apertures,

$$F(x) = \int_{w_1}^{w_2} \frac{\sin^2 w}{w^2}\,dw.$$

In this expression, if $\nu = 0$ and b = length of aperture,

$$w_1 = \frac{\kappa b}{2r}\phi_1(x) \text{ and } w_2 = \frac{\kappa b}{2r}\phi_2(x).$$

So long as

$$\frac{2\phi(x)}{r} < \frac{\lambda}{b},$$

$F(x)$ is nearly proportional to $\phi(x)$; that is, so long as the angle subtended by the source is less than the limit of resolution of a telescope with aperture b, the brightness is pro-

portional to the size of the object. For larger angles the proportionality may still be made to hold by a slight alteration in the focal adjustment; and to this degree of approximation we have

$$V^2 = \frac{[\int \phi(x) \cos kx\,dx]^2 + [\int \phi(x) \sin kx\,dx]^2}{[\int \phi(x)dx]^2} \quad . \quad . \quad . \quad (8)$$

If the source is symmetrical the second term vanishes, and the expression reduces to the original form.

It is possible that, in addition to the uses already mentioned, the "visibility-curve" may have an important application in the case of small spherical nebulæ. For from the form of this curve the distribution of luminous intensity in the globular mass may be inferred, which would furnish a valuable clue to the distribution of temperature and density in gaseous nebulæ.

When the source is so small as to be indistinguishable from a star, it would seem that this method is the only one capable of giving reliable information; but even in the case of bodies of larger apparent size it is equally applicable, may be made to give results at least as accurate as could be obtained by photometric measurements, and is far more readily applied.

XXIX. *On the Heating of Conductors by Electric Currents, and on the Electric Distribution in Conductors so heated.* By J. McCowan, *M.A., B.Sc., Assistant Lecturer on Natural Philosophy, University College, Dundee* *.

So far as I am aware, no problems in thermal distribution involving an internal generation of heat—such, for instance, as takes place in the passage of an electric current through a conductor—have hitherto been discussed. Fourier, the founder of the mathematical theory of thermal conduction, takes no account of possible internal sources of heat in forming his equations, and considers only problems in which the sources are superficial. The same may be said of Poisson, Lamé, Riemann, and others who have since applied and extended Fourier's methods. Thomson, in his synopsis of the mathematical theory †, has expounded Fourier's diffusion-analysis in a form directly applicable to cases where there are internal

* Communicated by the Author. Read before the Edinburgh Mathematical Society, January 9th, 1891.

† Appendix to article "Heat," *Encyc. Brit.* 9th edition.

sources of heat; but he omits the consideration of such sources in forming the differential equations of the motion.

In the case of heating by an electric current there is not only the thermal problem of finding the temperature at any point, but also the further electrical problem of determining the effect of the heating in changing the distribution of electric potential by the alteration which it produces in the conductivity. I am not aware that any solution of a problem of this latter class has hitherto been given.

In the following paper I have sought to discuss these problems more or less fully. The steady state which in general ultimately supervenes is considered in greater detail, not only because the mathematical treatment is much simpler, but also because it is of greater importance than the intermediate varying state; and for like reasons attention is chiefly given to the case of homogeneous isotropic conductors, but I have shown that many of the general results for these may be at once extended to heterogeneous ælotropic conductors.

It will be seen that the more general of the results at which I have arrived depend on and, in fact, are an almost immediate outcome of a remarkable transformation of which the thermal equation is susceptible even in its most general case, and by which the problem of electrical heating is immediately reduced to the ordinary case where there is no such heating.

It has been my object to develop the general theory rather than to seek results specially suitable to practical applications; but it will be seen that many of the results suggest electrical methods of experimentally examining the thermal characteristics of substances, and that the maximum theorems may be a useful guide where it is desired to produce high temperatures by electric means.

1. *Formation of the General Equations for the case of Heterogeneous Isotropic Conductors.*

Let V denote the electric potential and c the conductivity at time t at a point x, y, z in a heterogeneous isotropic conductor, then, there being no internal electrification, and for brevity using the notation

$$\nabla_c^2 = \frac{d}{dx}c\frac{d}{dx} + \frac{d}{dy}c\frac{d}{dy} + \frac{d}{dz}c\frac{d}{dz},$$

V must satisfy the equation

$$\nabla_c^2 V = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

Let ϑ denote the temperature, k the thermal conductivity,

and s the thermal capacity per unit volume at x, y, z, t ; then the rate at which heat accumulates per unit volume per unit time is

$$\nabla_k^2 \vartheta ;$$

and, by the law of Joule, the rate at which heat is generated by the current per unit volume per unit time is

$$jc\left\{\frac{d\mathrm{V}^2}{dx^2}+\frac{d\mathrm{V}^2}{dy^2}+\frac{d\mathrm{V}^2}{dz^2}\right\},$$

where j is the factor which reduces work expressed in the electrical units to its equivalent in the thermal units adopted ; hence, finally, the equation to be satisfied by ϑ will be

$$\frac{d}{dt}s\vartheta=\triangle_k^2\vartheta+jc\left\{\frac{d\mathrm{V}^2}{dx^2}+\frac{d\mathrm{V}^2}{dy^2}+\frac{d\mathrm{V}^2}{dz^2}\right\}. \quad . \quad . \quad . \quad \text{(B)}$$

The equations (A) and (B)—which it will be noted must be solved simultaneously in the general case, c being a function of ϑ,—in conjunction with the initial and boundary conditions, fully determine V and ϑ. As the initial and boundary conditions which may be imposed are almost entirely arbitrary, they need not be specially formulated here ; but it is to be noted that if ultimately they do not vary with the time, the thermal and electrical distributions will tend to stationary values, and ultimately the equation (B) to be satisfied by ϑ may be replaced by

$$\nabla_k^2\vartheta+jc\left\{\frac{d\mathrm{V}^2}{dx^2}+\frac{d\mathrm{V}^2}{dy^2}+\frac{d\mathrm{V}^2}{dz^2}\right\}=0. \quad . \quad . \quad \text{(C)}$$

When the conductor is homogeneous, and c, s, and k are taken, as within certain limits they may be without material error, independent of ϑ, the equations (A) and (B) reduce to

$$\nabla^2\mathrm{V}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(D)}$$

and

$$s\frac{d\vartheta}{dt}=k\nabla^2\vartheta+jc\left\{\frac{d\mathrm{V}^2}{dx^2}+\frac{d\mathrm{V}^2}{dy^2}+\frac{d\mathrm{V}^2}{dz^2}\right\}. \quad . \quad . \quad \text{(E)}$$

It is this case which will be discussed in the next four sections.

2. *The Ultimate Steady Distribution: Invention of Solvable Cases.*

As the direct problem of finding the solution for a body of given forms involves great difficulties, indirect methods giving us forms for which solutions may be directly obtained are of

considerable importance. Saint-Venant obtained many interesting and practically important solutions of problems on the torsion of elastic prisms in this way, and his results have been adapted by Thomson and Tait and others to problems in fluid motion in two dimensions. In what immediately follows I have applied this method to an interesting set of heating-problems, and have shown how the method can be considerably extended.

α. To find the steady distribution of temperature in a long cylindric bar carrying a current of strength q per unit area, its surface being maintained at a constant temperature, taken for convenience as the zero.

It is evidently only necessary to consider equation (E), which in this case reduces to

$$\frac{d^2\vartheta}{dx^2}+\frac{d^2\vartheta}{dy^2}+\frac{jq^2}{ck}=0,$$

and therefore we may take

$$\vartheta=\sigma-\tfrac{1}{2}(ax^2+by^2),$$

where σ is any solution of

$$\frac{d^2\sigma}{dx^2}+\frac{d^2\sigma}{dy^2}=0,$$

and $(a+b)=jq^2/ck$; and thus we shall have the solution for a bar whose surface is given by the equation

$$2\sigma=ax^2+by^2.$$

One or two examples only need be given :—

(i) Let the cross section be an ellipse, equation

$$b^2x^2+a^2y^2=a^2b^2.$$

Then clearly

$$\vartheta=\frac{jq^2}{2ck}\frac{a^2b^2}{a^2+b^2}\left\{1-\frac{x^2}{a^2}-\frac{y^2}{b^2}\right\},$$

and we see that the isothermal surfaces are similar concentric elliptic cylinders.

In the case of circular cross section this reduces to

$$\vartheta=jq^2\{a^2-x^2-y^2\}/4ck.$$

Again, when b is infinite, it reduces to the case of a flat plate of thickness $2a$, and

$$\vartheta=jq^2\{a^2-x^2\}/2ck.$$

(ii) Let the cross section be an equilateral triangle, and let a be the radius of the inscribed circle and α, β, γ the perpen-

diculars from a point on the three sides, then the solution may be written in the form

$$\vartheta = jq^2\alpha\beta\gamma/3ck\alpha.$$

It is interesting to extend two of these results—that for the bar or wire of circular cross section and that for the plate or approximately for any long flat strip—to suit the case where the surfaces having an emissivity e are exposed in air at temperature zero, instead of being maintained at that temperature. It is only necessary to raise the temperature by such an amount that the loss by emission will be equal to the rate of generation of heat by the current; and therefore for the circular wire the solution will be

$$\vartheta = jq^2\{a^2 - x^2 - y^2 + 2ak/e\}/4ck,$$

and for the flat strip,

$$\vartheta = jq^2\{a^2 - x^2 + 2ak/e\}/2ck.$$

In both these cases the ratio of the maximum temperature to the surface-temperature is $1 + ae/2k$.

β. To find the steady distribution of temperature in an annular conductor in which a current circulates, the surface being maintained at temperature zero.

Taking semipolar coordinates ϖ, ϕ, z, the equation (D) reduces to

$$d^2V/d\phi^2 = 0,$$

and therefore, if q denote the current per unit area at unit distance from the axis (that of z), (E) reduces to

$$\frac{d^2\vartheta}{d\varpi^2} + \frac{1}{\varpi}\frac{d\vartheta}{d\varpi} + \frac{d^2\vartheta}{dz^2} + \frac{jq^2}{ck\varpi^2} = 0;$$

and therefore we may take

$$\vartheta = \sigma - \frac{jq^2}{2ck}\{\log \varpi\}^2,$$

where σ is any solution of

$$\frac{d^2\sigma}{d\varpi^2} + \frac{1}{\varpi}\frac{d\sigma}{d\varpi} + \frac{d^2\sigma}{dz^2} = 0,$$

and this will be the solution for the ring formed by the revolution of the curve

$$\sigma = jq^2\{\log \varpi\}^2/2ck$$

about the axis of z.

For an example, take

$$\vartheta = \frac{jq^2}{2ck}\left\{\log\frac{b}{a}\log\frac{\varpi}{a} - \left(\log\frac{\varpi}{a}\right)^2\right\}:$$

then $\vartheta=0$ when ϖ is equal to a or b, and this is therefore the solution for a long tube or solenoid with current flowing round it.

The extension of Saint-Venant's method to this class of examples seems of some value, owing to the large part played by ring-shaped conductors in practical applications of electricity.

3. *Transformation of the Equations and General Method of Solution for the case of Homogeneous Conductors with Unvarying Conductivities &c.*

For brevity, put

$$U = \tfrac{1}{2}jcV^2 + k\vartheta,$$

then since identically

$$\nabla^2\tfrac{1}{2}V^2 = V\nabla^2V + \frac{dV^2}{dx^2} + \frac{dV^2}{dy^2} + \frac{dV^2}{dz^2},$$

and $\nabla^2V=0$ by (D), (E) may be reduced to

$$s\frac{dU}{dt} = k\nabla^2U, \quad . \quad . \quad . \quad . \quad . \quad . \quad (F)$$

and the general problem is thus reduced to the solution of (D) and (F) subject to the boundary conditions. These equations are of the same form as those for the steady and varying motion of heat in the ordinary case of no internal heating which have been very fully discussed ; it follows, therefore, that the more general problem of electrical heating is thus reduced to the same state of completeness as the more particular one. Thus, for example, if we can write down for a conductor of specified form an expression for the temperature at any point and time when every point of the surface is maintained at an arbitrary temperature, then we can also write it down when every point of the surface is maintained at an arbitrary temperature and potential ; and if there were no flux of heat over a specified portion of the surface, this would afford the solution for the case of no flux of heat or electricity over the same portion in the more general case.

General solutions may thus be obtained for the cuboid (Fourier), the sphere (Poisson), the circular cylinder (Mathieu), and in the case of steady motion for the ellipsoid (Lamé), various surfaces of revolution and cylindric surfaces. We may take for example, as the results can be written in very brief form, the

General Case of Steady Distribution in a Sphere.

Taking polar coordinates, r, θ, ϕ, let every point of the surface of the sphere $r=a$ be maintained at the arbitrary

potential $f_1(\theta\,.\,\phi)$ and temperature $f_2(\theta\,.\,\phi)$, then, as Poisson has shown,

$$V = \frac{1}{4\pi a}\int \frac{(a^2-r^2)\,f_1(\theta'.\,\phi')dS}{R^3},$$

where the integration extends over the surface of the sphere, and

$$R^2 = r^2-2ar\{\cos\theta\cos\theta'+\sin\theta\sin\theta'\cos(\phi-\phi')\}+a^2.$$

Therefore, further, as the surface-value of U will be $\frac{1}{2}jcf_1^2+kf_2$, we shall have

$$U = \frac{1}{4\pi a}\int \frac{(a^2-r^2)(\frac{1}{2}jcf_1^2+kf_2)dS}{R^3},$$

and finally

$$k\mathfrak{S} = U-\tfrac{1}{2}jcV^2,$$

where U and V have the values just written.

When, however, there is radiation from any part of the bounding surface, the ordinary results cannot be so directly generalized ; for the boundary equation in U is not then of quite the same form as that in $\mathfrak{S}$, being, when there is no flux of electricity across the surface,

$$-k\frac{dU}{d\nu} = e(U-\tfrac{1}{2}jcV^2),$$

where e is the emissivity, and ν the normal reckoned outwards.

The equation (E) may of course be reduced to the form of (F) by other methods or be discussed without such reduction, but the transformation chosen has the recommendation of being furnished by the electrical conditions and is specially related, as we shall see immediately, to an important class of cases of the steady state.

4. *The Steady State: a Special Solution.*

For the case of the ultimate steady distribution, (F) reduces to

$$\nabla^2 U = 0,$$

and since (D) is an equation of the same form, it follows that a solution is given by $U = A+BV$;

hence, determining the constants suitably, we obtain the following theorem :—

If any two parts of the surface of a conductor, throughout which the conductivities k and c are constant, are main-

tained at potentials V_1 and V_2 and at temperatures ϑ_1 and ϑ_2 respectively, and the remainder of the boundary is such that no flux of heat or electricity takes place across it, then, when the steady state supervenes, the equipotential surfaces will be isothermal and the temperature at any point will be given in terms of the initial (which is also the final) potential at that point by the formula

$$k\vartheta = \tfrac{1}{2}jc(V_2-V)(V-V_1) + k\{\vartheta_2(V-V_1)+\vartheta_1(V_2-V)\}/(V_2-V_1). \quad (1)$$

Thus, if the problem of the electrical distribution can be solved, the temperatures may be immediately obtained. From this theorem, as remarkable in generality as in simplicity, an extraordinary consequence results; for (1) may be written

$$\vartheta = \frac{\vartheta_2+\vartheta_1}{2} + \frac{jc}{8k}(V_2-V_1)^2 + \frac{k}{2jc}\left(\frac{\vartheta_2-\vartheta_1}{V_2-V_1}\right)^2 - \frac{jc}{2k}\left(V - \frac{V_2+V_1}{2} - \frac{k}{jc}\cdot\frac{\vartheta_2-\vartheta_1}{V_2-V_1}\right)^2,$$

which shows that ϑ has the maximum value

$$\vartheta' = \frac{\vartheta_2+\vartheta_1}{2} + \frac{jc}{8k}(V_2-V_1)^2 + \frac{k}{2jc}\left(\frac{\vartheta_2-\vartheta_1}{V_2-V_1}\right)^2 \quad . \quad . \quad (2)$$

over the surface for which V has the value

$$V' = \frac{V_2+V_1}{2} + \frac{k}{jc}\cdot\frac{\vartheta_2-\vartheta_1}{V_2-V_1}. \quad . \quad . \quad . \quad . \quad (3)$$

Thus the maximum temperature attained is entirely independent of the form or size of the body or its electrodes, depending only on the applied electromotive force (V_2-V_1), the temperatures ϑ_2 and ϑ_1 at which the electrodes are maintained, and the physical character of the body as defined by k and c.

It must be noted, however, that as V′ must lie between V_2 and V_1 in value, we have the condition that $2k(\vartheta_2-\vartheta_1)$ must lie between the limits $\pm jc(V_2-V_1)^2$ for a true maximum: when this condition is not satisfied, ϑ_2 and ϑ_1 will be the highest and lowest temperatures in the body.

When $\vartheta_2=\vartheta_1$ the condition for a maximum is always satisfied, and this case is perhaps more instructive than the more general one in which the natural gradient of temperature between ϑ_2 and ϑ_1 is superposed on that due to the electrical heating. Let then $\vartheta_2=\vartheta_1$, and for simplicity take this as the zero from which the temperature is reckoned, then (1) reduces to

$$\vartheta = \tfrac{1}{2}jc(V_2-V)(V-V_1)/k:$$

and therefore the surface of maximum temperature is the equipotential

$$V' = \tfrac{1}{2}(V_2 + V_1),$$

and the maximum temperature is

$$\vartheta' = jc(V_2 - V_1)^2/8k,$$

or

$$jcE^2/8k,$$

where E is the applied electromotive force.

From the examples considered in the following section a fair estimate of the time taken in establishing the steady state in this general case may be derived, and also of the disturbing effect produced by emission of heat from the bounding surface, which may be useful when it is difficult to obtain complete solutions by the methods of Section 3.

5. *Examples of the Varying State.*

When, as in the preceding section, the solution for the steady state can be found in the form

$$k\vartheta = A + BV - \tfrac{1}{2}jcV^2,$$

it will be convenient, in applying the method of Section 3 to find the solution for the intermediate varying state, to assume

$$U = k\vartheta + \tfrac{1}{2}jcV^2 - (A + BV),$$

so that the final state will be given by $U = 0$. U will still be determined by (F), and the initial condition will be

$$U = \tfrac{1}{2}jcV^2 - (A + BV),$$

if initially $\vartheta = 0$ throughout.

As an example, take the case of a cylindric bar of length $2l$, initially at temperature zero throughout, having its ends maintained at potentials $\pm V_0$, and at temperature zero, and its surface being impenetrable to heat.

The solution for the steady state is by last section,

$$k\vartheta = \tfrac{1}{2}jc(V_0^2 - V^2) = \tfrac{1}{2}jcV_0^2(1 - z^2/l^2),$$

the origin being taken at the middle of the bar. Now, noting that the ends are to be maintained at temperature zero, and expanding suitably by Fourier's Theorem, we get

$$\tfrac{1}{2}jcV_0^2\left(1 - \frac{z^2}{l^2}\right) = \tfrac{1}{2}jcV_0^2\,\frac{32}{\pi^3}\sum_0^\infty \frac{(-)^n}{(2n+1)^3}\cos\frac{(2n+1)\pi z}{2l},$$

which is the initial value of U. Hence, finding the general value of U, we have finally for ϑ,

$$k\vartheta = \tfrac{1}{2}jc(V_0^2 - V^2) - U$$

$$= \tfrac{1}{2}jcV_0^2\left(1 - \frac{z^2}{l^2}\right) - \tfrac{1}{2}jcV_0^2\frac{32}{\pi^3}\Sigma\frac{(-)^n}{(2n+1)^3}\epsilon^{-\frac{(2n+1)^2\pi^2kt}{4l^2s}}\cos\frac{(2n+1)\pi z}{2l}.$$

This series is very convenient, owing to its rapid convergence, so rapid that for many purposes it might be sufficient to take

$$\vartheta \doteqdot \frac{jcV_0^2}{2k}\left\{1 - \frac{z^2}{l^2}\right\}\left\{1 - \epsilon^{-\frac{\pi^2kt}{4l^2s}}\right\},$$

which is correct initially and finally, and always fairly approximate.

It is interesting to examine the effect of surface-emissivity on this solution. From Section 2 it is clear that unless the bar is very thick, the temperature may be taken as approximately constant throughout any cross section; making, then, this assumption, the thermal equation will be

$$s\frac{d\vartheta}{dt} = k\frac{d^2\vartheta}{dz^2} + \frac{jcV_0^2}{l^2} - ehe\vartheta,$$

where h is the ratio of the perimeter to the area of the cross section, and e the emissivity. Hence for the steady state we have

$$\vartheta = \frac{jcV_0^2}{l^2he}\left\{1 - \frac{\cosh z\sqrt{(he/k)}}{\cosh l\sqrt{(he/k)}}\right\}.$$

Proceeding almost exactly as in the previous case, we find, first,

$$1 - \frac{\cosh z\sqrt{(he/k)}}{\cosh l\sqrt{(he/k)}} = \frac{4}{\pi}\frac{he}{k}\Sigma\frac{(-)^n}{2n+1}\cdot\frac{\cos(2n+1)\pi z/2l}{(2n+1)^2\pi^2/4l^2 + he/k},$$

then generalize for U, and obtain finally

$$\vartheta = \frac{jcV_0^2}{l^2he}\left\{1 - \frac{\cosh z\sqrt{(he/k)}}{\cosh l\sqrt{he/k}}\right\}$$

$$-\frac{jcV_0^2}{l^2k}\frac{4}{\pi}\Sigma\frac{(-)^n}{2n+1}\cdot\frac{\cos(2n+1)\pi z/2l}{(2n+1)^2\pi^2/4l^2 + he/k}\epsilon^{-\left\{(2n+1)^2\pi^2k/4l^2 + he\right\}t/s}$$

We see that the effect of the emissivity is negligible when $4l^2he/\pi^2k$ is negligible compared with unity. We may take, adopting the usual C.G.S. units, $e \doteqdot 1/4000$ for polished surfaces, $k \doteqdot 1$ for copper, and 1/6 for iron: hence, for a bar of circular section, radius a and length L cms.,

$4l^2he/\pi^2k \doteqdot \cdot 000{,}05\,L^2/a$ for copper, and $\cdot 0003L^2/a$ for iron.

6. *General Case of a Homogeneous Isotropic Conductor.*

Since identically

$$\nabla_c^2 \tfrac{1}{2}\mathrm{V}^2 = \mathrm{V}\nabla_c^2\mathrm{V} + c\left\{\frac{d\mathrm{V}^2}{dx^2} + \frac{d\mathrm{V}^2}{dy^2} + \frac{d\mathrm{V}^2}{dz^2}\right\}$$

(B) reduces by means of (A) to

$$\frac{d}{dt}s\vartheta = \nabla_k^2\vartheta + \nabla_c^2 \tfrac{1}{2}j\mathrm{V}^2.$$

Now the conductor being initially homogeneous, s, c, and k are functions of ϑ only, therefore we may put

$$k = cf'(\vartheta) = c\frac{df}{d\vartheta}\ ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and thus (B) finally reduces to

$$\frac{d}{dt}s\vartheta = \nabla_c^2\{f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2\}. \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{G})$$

In the general case of varying movement the simultaneous equations (A) and (G) are utterly intractable except by methods of successive approximation, say, beginning with the assumption of s, c, and k, independent of ϑ. Passing, then, at once to the consideration of the steady state, we have, instead of (G),

$$\nabla_c^2\{f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2\} = 0. \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{H})$$

The general treatment of (A) and (H) is still extremely difficult, but these equations being of the same form, we can extend the method of Section **4** to give results similar to and equally general with those of that section, and, further, to obtain the final in terms of the initial distribution of potential. In fact

$$f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2 = \mathrm{A} + \mathrm{BV}$$

is an obvious solution, and therefore suitably determining A and B we find that :—

α. If any two parts of the surface of an initially homogeneous conductor for which $k = cf'(\vartheta)$ are maintained at potentials V_1 and V_2, and at temperatures ϑ_1 and ϑ_2 respectively, and the remainder of the boundary is such that there is no flux of heat or electricity across it, then, when the steady state supervenes, the equipotential surfaces will be isothermal, and the temperature at any point will be given in terms of the potential at that point by the formula

$$f(\vartheta) = \tfrac{1}{2}j(\mathrm{V}_2 - \mathrm{V})(\mathrm{V} - \mathrm{V}_1) + \{f(\vartheta_2)(\mathrm{V} - \mathrm{V}_1) + f(\vartheta_1)(\mathrm{V}_2 - \mathrm{V})\}/(\mathrm{V}_2 - \mathrm{V}_1). \quad . \quad (2)$$

From this, as in Section 4, we may deduce that :

β. The temperature will have a maximum value ϑ', given by

$$f(\vartheta')=\frac{f(\vartheta_2)+f(\vartheta_1)}{2}+\frac{j}{8}(V_2-V_1)^2+\frac{1}{2j}\left\{\frac{f(\vartheta_2)-f(\vartheta_1)}{V_2-V_1}\right\}^2 \quad (3)$$

over the surface for which the potential has the value

$$V'=\frac{V_2+V_1}{2}+\frac{1}{j}\frac{f(\vartheta_2)-f(\vartheta_1)}{V_2-V_1} \quad . \quad . \quad . \quad . \quad (4)$$

It should be noted that since k and c are essentially positive and finite, $f(\vartheta)$ must increase with ϑ continually and without limit.

In the important case where $\vartheta_1=\vartheta_2$ it is convenient to take the arbitrary constant in $f(\vartheta)$ such that

$$f(\vartheta_2)=f(\vartheta_1)=0,$$

and then the equations (2), (3), (4) become respectively

$$f(\vartheta)=\tfrac{1}{2}j(V_2-V)(V-V_1) \quad . \quad . \quad . \quad . \quad (2')$$

$$\begin{cases} f(\vartheta')=\tfrac{1}{8}j(V_2-V_1)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3') \\ V'=\tfrac{1}{2}(V_2+V_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4') \end{cases}$$

There is, however, a further problem to be solved ; the ultimate relation between V and ϑ has been obtained, but as the distribution of V is affected by the heating, there remains to be determined the final in terms of the initial distribution. The means of doing this is afforded by the foregoing results:—

Making use of (3) and (4), (2) may be written

$$f(\vartheta)=f(\vartheta')-\tfrac{1}{2}j(V-V')^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\therefore \quad V=V'\pm\sqrt{(2/j)}\sqrt{\{f(\vartheta')-f(\vartheta)\}}.$$

$$\therefore \text{ by (1)}, \quad c\frac{dV}{d\vartheta}=\frac{\mp k}{\sqrt{\{2jf(\vartheta')-2jf(\vartheta)\}}}=F'(\vartheta), \text{ say}, \quad (6)$$

where the upper sign is to be taken in the space between the electrode at potential V_2 and the surface of maximum temperature, and the lower sign from the latter surface to the other electrode.

By means of (6), (A) reduces to

$$\nabla^2F(\vartheta)=0.$$

Now if V_0 denote the potential at any point of the same conductor when at the same temperature throughout, as it would be, if initially so, immediately after the application of the

electromotive force $V_2 - V_1$ before it had time to be heated by the current,

$$\nabla^2 V_0 = 0,$$

for c and k are constant since the temperature is uniform. Thus $F(\vartheta) = A + BV_0$, where A and B have to be determined to suit the boundary conditions. Now $F(\vartheta)$ is by (6) a known function of ϑ, since k and $f(\vartheta)$ are known functions of ϑ, except as regards an arbitrary constant. It is here convenient to take this such that $F(\vartheta') = 0$, and to denote by $-\lambda$ and μ respectively the values of $F(\vartheta)$ at the two electrodes, which are maintained finally at the temperatures ϑ_1 and ϑ_2. Hence, determining A and B, we have finally

$$(V_2 - V_1)F(\vartheta) = (\lambda + \mu)V_0 - (\lambda V_2 + \mu V_1). \quad . \quad (7)$$

Thus the final temperature ϑ, and therefore also by (2) the final potential, is determined in terms of the initial potential in the same conductor uniformly heated, which may be found by the ordinary methods.

In the case $\vartheta_2 = \vartheta_1$, which is really the fundamental one, and from which the more general case could have been derived, we see by (6) that λ will be equal to μ, and therefore (7) will become

$$(V_2 - V_1)F(\vartheta) = 2\lambda\{V_0 - \tfrac{1}{2}(V_1 + V_2)\}. \quad . \quad . \quad (7')$$

Thus, comparing (7′) and (4′), we see that the surface of maximum temperature has initially and finally the same potential, the mean of that of the electrodes, and being, therefore, independent of k and c, its form and position will be the same for all homogeneous isotropic conductors which have the same form of boundary and electrodes.

In the general case, we see that surfaces which are equipotential initially are also so finally, but the values of their potentials are in general different. It is not, however, to be supposed that equipotentials remain so during the intermediate state ; in fact, it is easy to show that they do not, except in the particular cases where they are a set of planes, spheres, or circular cylinders. It is also obvious that the initial and final coincidence of equipotentials would in general be destroyed by any emission from the bounding surface, the equipotentials then also ceasing to be isothermal.

7. *Special Results for Cylindric Surfaces.*

The methods of Sections 4 to 6 may be slightly modified to give in the case of cylindric surfaces a new set of theorems analogous to those of these sections, but in which current takes the place of potential, and resistance of conductivity.

Let Q be the current-function, and $\rho = 1/c$ the resistivity, then

$$\rho\left\{\frac{d\mathrm{Q}^2}{dx^2} + \frac{d\mathrm{Q}^2}{dy^2}\right\} = c\left\{\frac{d\mathrm{V}^2}{dx^2} + \frac{d\mathrm{V}^2}{dy^2}\right\}$$

$$\nabla_\rho{}^2\mathrm{Q} = 0 = \nabla_c{}^2\mathrm{V}.$$

Thus the properties of Q and ρ are like those of V and c. Put then

$$k = \rho f_0'(\vartheta), \quad \text{and} \quad \frac{\mp k}{\sqrt{\{2jf_0(\vartheta') - 2jf_0(\vartheta)\}}} = \mathrm{F}_0'(\vartheta),$$

where ϑ' is the maximum value of ϑ (see below), substitute in the investigation of Section 6, f_0 for f, F_0 for F, Q for V, and ρ for c, adapt the language similarly, and the following theorems are immediately obtained.

Call the lamina enclosed between two cylindric surfaces a cylindric sheet when unlimited, and a cylindric strip when it is limited by two planes (its sides) cutting it orthogonally. If the cylindric sheets are given by the values Q_2 and Q_1 of the current function, then the whole current per unit breadth between them, $\mathrm{Q}_2 - \mathrm{Q}_1$, may be denoted by C, and the parts flowing on each side of a point on the sheet Q, viz., $\mathrm{Q}_2 - \mathrm{Q}$ and $\mathrm{Q} - \mathrm{Q}_1$ by C_2 and C_1 respectively.

α. If the surfaces of a cylindric sheet, or strip with impermeable sides, of a homogeneous conductor for which $k = \rho f_0'(\vartheta)$, are maintained at temperature zero, and a current C per unit breadth is maintained through it, then ultimately the current-sheets will be isothermal, and the temperature at any point will be given in terms of the parts C_1 and C_2 of the whole current C which flow on each side of the point, by the formula

$$f_0(\vartheta) = \tfrac{1}{2}j\mathrm{C}_1\mathrm{C}_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the temperature will have a maximum value ϑ' given by $f_0(\vartheta') = j\mathrm{C}^2/8$ over the surface which equally divides the current (the same initially and finally).

Finally, if Q_0 be the initial value of Q at any point, and 2λ is the difference in the value of $\mathrm{F}_0(\vartheta)$ at the two boundaries, then

$$(\mathrm{Q}_2 - \mathrm{Q}_1)\,\mathrm{F}_0(\vartheta) = 2\lambda\{\mathrm{Q}_0 - \tfrac{1}{2}(\mathrm{Q}_1 + \mathrm{Q}_2)\}. \quad . \quad . \quad (2)$$

Thus the final temperature, and therefore also by (1) the final current distribution, is given in terms of the initial current-distribution which may be investigated by the ordinary methods.

For simplicity, the case of zero-bounding temperatures has been taken above, but the general results of Section 6 may be

transformed equally directly. The case of constant conductivities is, of course, obtained directly from the above by putting $f_0(\vartheta) = k\vartheta/\rho$; and it should be noted that, owing to the conjugate properties of the current and potential functions, the general method of Section **3** gives easily, on Fourier principles, the solution for the case of arbitrary (two-dimensional) surface-temperatures, for any strip for which these functions are known. As an example, take a strip for which V and Q are the potential and current functions, its boundaries being given by $\pm Q_0$ and $\pm V_0$, these being maintained at zero temperature, and the remaining plane sides being impermeable. Proceeding as in Section **3**, with the modification suggested in Section **5**, we take

$$U = k\vartheta - \tfrac{1}{2}jc\{V_0^2 - V^2\}, \text{ and } \therefore \nabla^2 U = 0.$$

Expanding next by Fourier's theorem, having the boundary-conditions in view, we get

$$\tfrac{1}{2}jc(V_0^2 - V^2) = \tfrac{1}{2}jcV_0^2 \cdot \frac{32}{\pi^3} \Sigma \frac{(-)^n}{(2n+1)^3} \cos(2n+1)\pi V/2V_0.$$

Hence we obtain U, and therefore finally

$$k\vartheta = \tfrac{1}{2}jc(V_0^2 - V^2) - \tfrac{1}{2}jcV_0^2 \frac{32}{\pi^3} \Sigma \frac{(-)^n}{(2n+1)^3} \frac{\cosh(2n+1)\pi\rho Q/2V_0}{\cosh(2n+1)\pi\rho Q_0/2V_0} \cos(2n+1)\pi V/2V_0.$$

8. *General Case of Heterogeneous Æolotropic Conductor.*

The equation satisfied by V is, in its most general form,

$$\frac{d}{dx}\left\{c_1\frac{dV}{dx} + p_3\frac{dV}{dy} + q_2\frac{dV}{dz}\right\} + \frac{d}{dy}\left\{q_3\frac{dV}{dx} + c_2\frac{dV}{dy} + p_1\frac{dV}{dz}\right\} + \frac{d}{dz}\left\{p_2\frac{dV}{dx} + q_1\frac{dV}{dy} + c_3\frac{dV}{dz}\right\} = 0.$$

$$\text{say, } \nabla^2_{(c.p.q)} V = 0. \quad . \quad . \quad . \quad . \quad . \quad (A')$$

but probably the p's are identical with the q's*.

The equation satisfied by ϑ is

$$\frac{d}{dt}s\vartheta = \nabla^2_{(k.r.s)}\vartheta + j\left\{c_1\frac{dV^2}{dx^2} + c_2\frac{dV^2}{dy^2} + c_3\frac{dV^2}{dz^2} + (p_1+q_1)\frac{dV}{dy}\frac{dV}{dz} + (p_2+q_2)\frac{dV}{dz}\frac{dV}{dx} + (p_3+q_3)\frac{dV}{dx}\frac{dV}{dy}\right\},$$

* Maxwell's 'Electricity and Magnetism,' Part ii. chap. viii.

and by means of the preceding this reduces to

$$\frac{d}{dt}s\vartheta = \nabla^2_{(k\,.\,r\,.\,s)}\vartheta + \nabla^2_{(c\,.\,p\,.\,q)}\tfrac{1}{2}j\mathrm{V}^2.$$

Hence, if we assume, as experiment to some extent at least entitles us, that

$$(k\,.\,r\,.\,s)(1\,.\,2\,.\,3) = (c\,.\,p\,.\,q)(1\,.\,2\,.\,3)f'(\vartheta)$$

respectively, this further reduces to

$$\frac{d}{dt}s\vartheta = \nabla^2_{(c\,.\,p\,.\,q)}\{f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2\}. \quad . \quad . \quad . \quad (\mathrm{G}')$$

In the case where $f'(\vartheta)$ is a constant, m say, and s is also independent of ϑ, we have, putting $\mathrm{U} = f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2$,

$$s\frac{d\mathrm{U}}{dt} = m\nabla^2_{(c\,.\,p\,.\,q)}\mathrm{U}, \quad . \quad . \quad . \quad . \quad (\mathrm{F}')$$

which has the same form as the ordinary equation for the movement of heat in a heterogeneous conductor when there is no internal heating, and hence, as in Section **3**, we see how results for this case may be generalized to include electric heating.

In any case, however, we see, comparing (A′) and (G′), that a solution for the steady state is given by

$$f(\vartheta) + \tfrac{1}{2}j\mathrm{V}^2 = \mathrm{A} + \mathrm{BV},$$

and thus the theorems (α) and (β) of Section **6** are immediately extended to heterogeneous conductors.

If we now assume, further, more or less on the warrant of experiment, that

$$(c\,.\,p\,.\,q)(1\,.\,2\,.\,3) = (c_0\,.\,p_0\,.\,q_0)(1\,.\,2\,.\,3)\phi(\vartheta)$$

respectively, where the zero subscripts refer to the values at the temperature zero, and put

$$\mathrm{F}'(\vartheta) = \mp\phi(\vartheta)f'(\vartheta)/\sqrt{\{2jf(\vartheta') - 2jf(\vartheta)\}},$$

where ϑ' is the maximum temperature, and the signs are to be taken as in (6), Section **6**, we get

$$\nabla^2_{(c_0p_0q_0)}\mathrm{F}(\vartheta) = 0.$$

Again, if V_0 denote the potential with the same surface-conditions, but $\vartheta = 0$ throughout the conductor,

$$\nabla^2_{(c_0p_0q_0)}\mathrm{V}_0 = 0.$$

Therefore $\mathrm{F}(\vartheta) = \mathrm{A} + \mathrm{BV}_0$, or definitely, as in Section **6** (7′),

$$(\mathrm{V}_2 - \mathrm{V}_1)\mathrm{F}(\vartheta) = 2\lambda\{\mathrm{V}_0 - \tfrac{1}{2}(\mathrm{V}_1 + \mathrm{V}_2)\},$$

which completes the solution, and leads to results similar to those of the latter portion of Section 6, *e. g.*, that surfaces equipotential initially are also so finally, and the surface of maximum temperature has the same potential, the mean of the electrodes, initially and finally.

Similarly we may extend the corresponding results of Section 7.

From the maximum theorems which have been obtained, a general result as to the superior limit of the temperature in any part of a conductor is easily derived. It is only necessary to notice that any further escape of heat than is allowed for in these theorems cannot raise the temperature at any point, but must, on the contrary, lower it more or less; hence:—

If in any conductor heated by a current a closed surface, or two surfaces which, by cutting through the boundary, enclose a portion of the body between them, be taken, then the highest temperature in the enclosed portion cannot be greater than the highest temperature on the closed surface or on the cross-sectional surfaces—provided, in this latter case, no heat flows into the enclosed portion through the remainder of the boundary—by more than, though it may be as much as, the value ϑ', which is given by $f(\vartheta')=jE^2/8$, where E is the greatest difference of potential between any two points of the closed surface or pair of surfaces, and $f'(\vartheta)$ is the ratio of the thermal and electric conductivities.

By "any conductor" is, of course, to be understood, in the general case of heterogeneity, one with conductivities subject to the limitations introduced in this Section.

A similar result in the case of two dimensions may be at once derived from the maximum theorem of Section 7, but it is unnecessary to state it.

XXX. *The Influence of the Bending of Magnetic Needles on the apparent Magnetic Dip.* *By* Arthur Schuster, *F.R.S.**

IN Maxwell's Treatise on 'Electricity and Magnetism,' vol. ii. page 117, the following passage occurs:—

"Dr. Joule finds that the needle should not be more than five inches long. When it is eight inches long, the bending of the needle tends to diminish the apparent dip by a fraction of a minute."

I have not been able to find in any of Joule's writings a passage on which the above statement could be founded. Such a passage may have escaped me; but it is not impossible that

* Communicated by the Author.

Maxwell had some private information from Joule, in which unpublished experiments on the bending of magnetic needles were referred to.

At any rate the question seems worthy of consideration, because for a number of years the Greenwich Observatory has published observations made with needles 9, 6, and 3 inches long, which show a systematic difference in the observed dip amounting to more than a minute of arc between the longest and shortest needles.

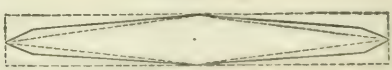
It is clear that the mere displacement of the ends of the needle by the bending is eliminated by the method of observation which is uniformly adopted, but in addition there is the effect alluded to by Maxwell, which is not so easily disposed of. The bending of the needle causes a displacement of the centre of gravity, and a little reflection will show that this displacement must cause a diminution in the apparent dip. Let h be the distance of the centre of gravity from the axis of rotation, ϕ the dip, and δ the small angle through which the needle is turned by the displacement of the centre of gravity. Equating the moments of the forces which balance in the position of equilibrium, we find

$$mgh \sin \phi = \mathrm{TM}\delta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

M represents the magnetic moment of the needle, and T the earth's magnetic force. In order to form an estimate of the angle δ, we must take account therefore of the displacement h and the magnetic moment of the needle. It is assumed that the needle when it is straight has its centre of gravity in the axis of rotation. Errors due to non-fulfilment of that condition are eliminated by the method of observation.

The needles used at Greenwich have the form shown in fig. 1. It would not repay the trouble to determine the

Fig. 1.



bending for such a shape. It will be sufficient to carry out the calculations for the shapes indicated by the dotted lines; that is to say, to imagine needles having cross sections which are either uniform or diminish uniformly.

The effect of pointed needles will be found to be smaller than that of rectangular magnets; and we shall be justified in assuming that needles having the actual shape in use will give an intermediate result.

The amount of bending of rectangular bars is well known,

and we may confine ourselves to the case of the pointed needles, for which the calculation is very simple.

We take a pointed needle of unit thickness and half length l, and find in the first place the equation of its axis when it is in a horizontal position and subject to its own gravity alone. Let the axis of x be horizontal, and that of y downwards. If a cross section of the needle is taken at a point P, the bending-couple at the section is that of the weight of the pointed end multiplied by the distance of the centre of gravity of the end from the cross section, or

$$g\rho \frac{v(l-x)}{2} \cdot \frac{(l-x)}{3}.$$

In this equation v represents the width of the needle at the point P.

If a is the width at the origin,

$$vl = a(l-x),$$

and the bending-couple becomes

$$\frac{g\rho}{6} \frac{a}{l} (l-x)^3.$$

If Y is Young's modulus of elasticity, the resistance to the bending will be $\mathrm{Y} \frac{v^3}{12}$. Substituting the value of v in terms of z, the differential equation for the axis becomes

$$\frac{dy^2}{dx^2} = \frac{2l^2}{a^2\mathrm{Y}} \cdot g\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence the curvature is constant and the needle takes up a circular shape. The integral of equation (1), taking account of the conditions holding at the origin, is:—

$$y = \frac{l^2}{a^2\mathrm{Y}} g\rho x^2.$$

The distance h between the centre of gravity and the axis is now obtained in the usual manner.

$$h = \frac{\int_0^l yv\,dx}{\int_0^h v\,dx} = \frac{l^2 g\rho}{a^2\mathrm{M}} \frac{\int_0^l x^2(l-x)\,dx}{\int_0^l (l-x)\,dx};$$

from which it follows that

$$h = \frac{g\rho l^4}{6\mathrm{Y}a^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the calculation is conducted in the same way for straight bars of uniform cross section a, the result is

$$h = \frac{3}{5}\frac{g\rho l^4}{Y a^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence for pointed needles of cross section a the displacement of the centre of gravity is smaller in the ratio of 18 to 5 as compared with needles having an uniform cross section a throughout.

To apply the results obtained to our problem, we must multiply the value of h by $\cos\phi$, because if the needle is not horizontal the gravitational force has to be resolved at right angles to the needle in order to obtain that component which serves to bend it.

We substitute the value h from equation (3) into (1) and may thus calculate the correction of the dip due to bending by the formula

$$\delta = \frac{mg^2\rho l^4}{6MYTa^2}\sin\phi\cos\phi = \frac{g^2\rho^2 l^4}{6YTa^2}\cdot\frac{V}{M}\sin\phi\cos\phi,$$

where V is the volume occupied by the needle.

If the dimensions of the needle are known all quantities except Young's modulus and the magnetic moment may be introduced into the equation. As regards Young's modulus, the values given for it lie between $2{\cdot}1\times10^{12}$ and $2{\cdot}5\times10^{12}$. I take the latter number, as it is my object to show that bending is sufficient to account for the diminished dip of the longer needles, and I wish therefore to *underrate* the effect of bending. It is more difficult to form an estimate of the magnetic moment per unit volume or M/V. Kohlrausch, in his 'Physical Measurements,' states that with thin long needles values as high as 785 may be obtained, but that such magnets as are used in Physical Laboratories seldom show a greater magnetic moment than 312 C.G.S. per unit volume. The shape of dipping-needles and the method of magnetization does not render it probable that these needles reach the lower number given by Kohlrausch, for the central parts of the needle will add more to the weight than to the magnetic moment. If, therefore, we make $M/V = 320$, this will probably be above the correct value.

With these numbers I have calculated the value of δ, taking the width and length of the needles used at Greenwich. I have to acknowledge the kindness of the Astronomer Royal in giving me detailed information on the dimensions and shape of the needles used at the Royal Observatory. The

following Table embodies the results of the calculation. Columns I. and II. give the length and width of the needles in inches. Column III. gives the diminution of dip due to bending of needles, having a greatest width equal to that of the Greenwich needles, but tapering uniformly towards the end, as shown in fig. 1. Column IV. shows what the diminution in dip would be if the needles had everywhere the same width a. It is reasonable to suppose that needles of the shape actually used would give values for δ intermediate between those of columns III. and IV. Column V. gives the difference in dip between the two longer needles and the one having a length of only three inches, the bending of which may be neglected. To obtain this difference I have taken the mean dip of the three sets of needles for the six years 1882 to 1887, as published in the Annual Reports of the Greenwich Observatory ; its value is entered into column VI.

I.	II.	III.	IV.	V.	VI.
$2l$.	a.	δ. (needles.)	δ. (bars.)	δ. (Greenwich.)	Mean Dip.
3	·33	$''$ 5	$'$ 0 $''$ 2	$'$ $''$	$^\circ$ 67 $'$ 29 $''$ 57
6	·39	7	0 24	0 26	67 29 23
9	·47	23	1 19	1 00	67 28 57

Considering that we have throughout underrated the effect of bending, especially by assuming a value for the magnetic moments which is in all probability too high, the figures leave no doubt that the difference in the dip shown by needles of different lengths can be accounted for by their bending. The calculated value for pointed needles is about three times too small ; that for needles of uniform cross section gives results closely agreeing with the observed differences in the dip ; while the actual shape of the needles agrees more closely with that of uniform bars than with that of pointed needles.

The results of calculation quite justify Joule's remark as to the importance of using short needles to avoid the introduction of appreciable errors ; and the question arises whether long needles are entirely to be rejected, as is done in most Observatories, or whether a correction should be made for the diminution of the dip. The difficulty in measuring angles to a sufficient accuracy is increased if the needles are as short as the shortest Greenwich needles, and hence there is some

advantage in retaining the longer ones. The bending might be diminished to an almost inappreciable amount by having the needles about three times as wide, but it would then become more difficult to magnetize them strongly. If the magnetic moments of the needles were measured before every observation, the error due to bending could be calculated to a sufficient degree of accuracy, as Young's modulus will not differ much in different specimens of steel used for magnets. This course would, however, entail a good deal of trouble, and it almost seems to me as if an empirical correction would answer the purpose almost equally well. We might, for instance, determine the correction to be applied in any particular year with sufficient accuracy by finding the mean difference of dip shown by the needles in a certain number, say five, of preceding years. As the influence of bending for the three-inch needles is negligible, and as the magnetic properties of the needles, which are always magnetized in the same way, will probably not alter during a course of five years, a fairly accurate correction may be deduced. Thus, for instance, during the five years 1882–86 the mean dip of the needles in the order of their length was 67° 30′ 30″; 67° 30′ 00″; 67° 29′ 35″. We deduce a correction of 55″ for the longest needles, and one of 30″ for the intermediate ones. The observed dip in 1887 was 67° 27′ 13″; 67° 26′ 20″; 67° 25′ 45″; and, applying the correction, we find for the three needles the now closely-agreeing values of 67° 27′ 13″, 67° 26′ 50″, 67° 26′ 40″. The mean of these three values, viz. 67° 26″ 54″, will probably be as near the truth as the errors of observation will allow.

I have not brought this matter forward in any spirit of criticism towards the Greenwich observations. The fact that the small effect of bending shows itself persistently from year to year to a nearly equal degree, is in itself a proof of the excellency of the observations. The manner in which the magnetic records are reduced, and the form in which they are published by the Greenwich authorities, may well serve as a model to other Observatories. But as there seems no doubt that the accuracy which is aimed at in the dip-observation is appreciably affected by the cause of error which Joule has pointed out, it seems to me advisable to eliminate that error. The exact way in which the correction is carried out may well be left to the proper authorities.

XXXI. *The Solution of a Geometrical Problem in Magnetism.* *By* T. H. Blakesley, *M.A.**

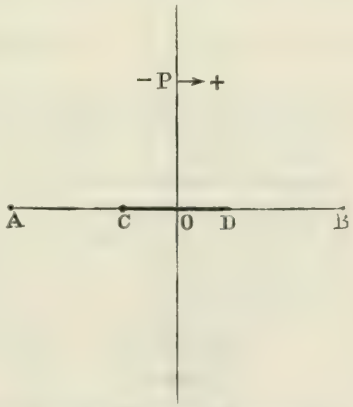
THE points in the field of a magnet usually chosen for quantitative experiments, such as the determination of H, or the control of a galvanometer-needle, lie either in the axis of the magnet produced, or the equatorial plane. This arises from the very simple expressions for the field in terms of the moment of the magnet, and its distance from the point considered, in these two cases. But in either of these cases the exact value depends not merely upon these facts, but also upon the distance between the poles; and this latter can rarely, if ever, be taken to be the entire length of the magnet. Either some such rule as the lopping-off, in imagination, of a fraction of the length, is applied, or the virtual distance between the poles is expressed as an unknown quantity to be determined by additional experiment.

It is easy also to calculate the direction and magnitude of the field at a point whose position relatively to the two poles is given. But the following proposition is, at first sight, of a more difficult order.

"Given the two poles of a magnet, and a straight line intersecting at right angles its axis produced at a given point, to determine at what point this line is parallel to the field."

The solution of this question may be of some scientific interest; because if we know the point experimentally, we can determine the length between the virtual poles. But the question is important practically from its bearing upon that of the deviation of a ship's compass in some cases.

Fig. 1.



Suppose A B a long uniformly magnetized rod having poles at A and B (say A is a north pole), and O P its equatorial plane. Then the field at P is always parallel to A B, and in the direction of those letters, which call the positive direction. Suppose a piece C D cut away so as to leave a gap having same equator.

At C a south pole is developed, and at D a north pole.

* Communicated by the Physical Society: read November 28, 1890.

These two poles produce a field at P parallel to D C, and in the negative direction.

If the point is in the neighbourhood of O, the two inner poles will be dominant and the field negative; but if P is very remote from O, the poles A and B will be dominant, and the field positive. There must therefore be some position where the field vanishes, and the two rods A C, D B would produce no deviation on a compass at that point, in whatever direction the head of the ship carrying the system pointed.

Such permanent magnets would produce what is called semicircular deviation on a compass situated at any distance but this critical one from O; that is, through one semicircle the deviation would be easterly, and through the remaining semicircle westerly; but these semicircles would each have the deviation produced in it changed in sign if this critical point is transgressed. If, however, the rods A C, D B are of soft iron, liable to magnetization by the action of the horizontal component of the earth's field, the general effect is that the direction of the deviation changes sign after every *quadrant*, each pair of *opposite* quadrants having one kind of deviation, easterly or westerly; and in this case the actual sign for each pair of opposite quadrants depends upon the position of the compass relative to this critical position.

This application may serve to excuse me for bringing forward an easy method of practically finding this point.

It is clear that the point is one for which the field due to either magnet, A C or D B, alone, would be entirely along O P, *i. e.* at right angles to the axis of the magnet.

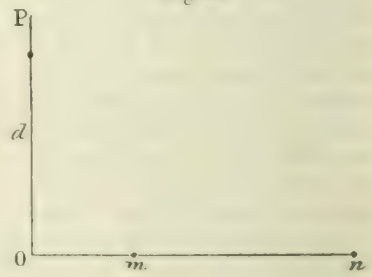
The Solution.

Let $n\,m$ be the position of the poles of a magnet, and P a point situated at distance d from O, O being in the axis of the magnet produced, and P O being perpendicular to O $m\,n$.

Let the distance

$$On = n,$$
$$Om = m.$$

Fig. 2.



Let p be the numerical value of the poles m and n.

Then, writing down the condition that the component parallel to the magnet of the field produced at P by p at m shall be

equal and opposite to the same thing produced by p at n, we obtain

$$\frac{m}{(d^2+m^2)^{\frac{3}{2}}} = \frac{n}{(d^2+n^2)^{\frac{3}{2}}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as the equation to find d, all the other measurements being known.

Manipulating this expression, we have at length

$$\left(\frac{d^2}{2mn}\right)^3 - \frac{3}{4} \times \frac{d^2}{2mn} - \frac{1}{4} \times \frac{m^2+n^2}{2mn} = 0. \quad . \quad . \quad (2)$$

Now it happens that in hyperbolic trigonometry we have

$$\cosh^3\theta - \tfrac{3}{4}\cos\theta - \tfrac{1}{4}\cosh 3\theta = 0. \quad . \quad . \quad . \quad . \quad (3)$$

If, therefore, we make

$$\frac{m^2+n^2}{2mn} = \cosh 3\theta, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

we have also

$$\frac{d^2}{2mn} = \cosh\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By means, therefore, of the table of hyperbolic sines and cosines which this Society has recently published, we can easily determine d. .

We can deduce the distance of the poles apart, by applying this proposition inversely.

It is of course very easy to arrive at this state of things practically with a magnet.

Suppose we arrange a small magnetometer-needle in the meridian, and notice the position of the light-beam on a scale in an ordinary way.

Find the direction of the axis of the needle by the condition that a long magnet laid in that line will not affect the position of the spot of light ; then place that magnet, or any other, at right angles to this position and move it in the direction of its length until again the spot of light is at its old place. No torsion affects these observations; indeed, the real meridian need not have been the direction found.

Then, obviously, of the various quantities quoted in the problem, we are in direct possession of d and $m+n$ (the latter because the middle point of the magnet is distant $\frac{m+n}{2}$ $(=l)$,

perpendicularly from the axis of the magnetometer-needle); but the pole-distance $\overline{m-n}=2a$ is only implicitly known.

Its value may be deduced from the equations (4) and (5); thus

$$\frac{\overline{m-n}}{m+n} \text{ or } \frac{2a}{2l}=\frac{a}{l}=\tanh\frac{3\theta}{2},$$

where

$$\frac{l}{d}=\sqrt{\frac{\cosh 3\theta+1}{4\cosh\theta}}.$$

The latter function is not hard to deduce from the tables.

Experiments on this plan showed that the virtual distance between the poles soon approaches the full length of the magnet.

It remains to give the expression for the field under the circumstances. It is

$$\frac{4\mathrm{M}}{d^3}\ \frac{\cosh^2\theta}{(4\cosh^2\theta-1)^{\frac{3}{2}}},$$

where M is the moment, or $p(n-m)$.

It will be noticed that we have $\frac{l}{d}$ at our disposal if we allow d to vary, *i. e.* one degree of freedom. Suppose, therefore, we arrange to simplify the expression for the field by putting

$$\cosh^2\theta=\frac{5}{4}.$$

Then the field $=\frac{5\mathrm{M}}{8d^3}$;

but at the same time, since

$$\cosh\theta=\frac{\sqrt{5}}{2},$$

$$\cosh 3\theta=\sqrt{5},$$

$$\therefore \frac{l}{d}=\sqrt{\frac{\cosh 3\theta+1}{4\cosh\theta}}=\left(\frac{5^{\frac{1}{2}}+1}{2\times 5^{\frac{1}{2}}}\right)^{\frac{1}{2}}$$

$$=\left(\frac{1}{2}+\frac{\sqrt{5}}{10}\right)^{\frac{1}{2}}$$

$$=\cdot 850651.$$

Let $\tan \phi = \frac{l}{d}$, then

$$\phi = 40^\circ\ 23'\ 10'',$$

and we must keep the middle point of the magnet on the line making this angle with the meridian.

XXXII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 145.]

January 21, 1891.—A. Geikie, Esq., LL.D., F.R.S., President, in the Chair.

THE following communication was read:—

"On the Age, Formation, and Successive Drift Stages of the Valley of the Darent; with Remarks on the Palæolithic Implements of the District, and on the Origin of the Chalk Escarpment." By Professor Joseph Prestwich, D.C.L., F.R.S., F.G.S., &c.

i. *General Character and Age of the Darent Valley.*—The river is formed by the union of two streams, the main one flowing east from near Limpsfield, the other west from near Ightham, parallel with the ranges of Lower Greensand and Chalk, and flows northward into the Thames. The first indent of the valley was subsequent to the deposition of the Lenham Sands, and indeed to the Red Clay with flints and the old implement-bearing drift with which this is associated; and the same remark applies to a system of smaller valleys starting near the crest of the escarpment and running into the Thames.

ii. *The Chalk Plateau Drifts and associated Flint Implements.*—Since the publication of the author's Ightham paper, Mr. Harrison and Mr. De B. Crawshay have found implements mostly of rude type (though a few are as well finished as those of Abbeville) in numerous localities on the plateau, where, owing to the gradients, the difference of level between plateau and valley-bottom is much greater than at Currie Farm. Evidence derived from the character and conditions of preservation of these implements is adduced in favour of their great antiquity.

iii. *The Initial Stages of the Darent Valley.*—The author has previously shown that in early Pliocene times a plain of marine denudation extended over the present Vale of Holmesdale, and that in pre-glacial times the plain was scored by streams flowing from the high central Wealden ranges. These streams centred in the Darent, and the excavation of the present valley then commenced. There is a gap in the

sequence between the pre-glacial drifts and the earliest post-glacial drifts of the valley, which is probably covered by the extreme glacial epoch. It was a time of erosion, rather than of deposition in this area. Of the earliest drift of the Darent valley, little has escaped later denudation. The bank of coarse gravel on the hill on the west side of the valley between Eynsford and Farningham, certain flint-drifts in the upper part of the valley, and a breccia of chalk-fragments on the hill west of Shoreham, may be referred to this period.

iv. *The High-Level or Limpsfield Gravel Stage.*—The gravel at Limpsfield occurs on the watershed between the Darent valley and the Oxsted stream, but the author agrees with Mr. Topley that the gravel belongs to the Darent system, and Westheath Hill may be part of the original ridge separating the two valleys. This gravel is post-glacial, and the denudation of the area had made considerable progress at the time of its formation, for the Chalk escarpment rises 200–300 feet, and the Lower Greensand 100–200 feet above the gravel-bed. The author traces outliers of this gravel down the valley at lower and lower points to the Thames valley at Dartford, and correlates it, not with the high plateau-gravel, but with the High-level gravel of the Thames valley, and shows that its composition indicates that it is derived from the denudation of the Chalk and Tertiary beds. Mr. A. M. Bell has discovered numerous implements in it, mostly of the smaller St. Acheul type, and the author hopes that they will soon be described by their discoverer. These implements agree in general type with the "Hill group" of the Shode valley, and not with the older group of the Chalk plateau, or those of the lower levels of the Thames and Medway.

v. *Contemporaneous Drift of the Cray Valley.*—Implements of this age have been found by Mr. Crawshay and by Mr. P. Norman, near Green Street Green, in gravel which is more than 100 feet below the Red Clay of the plateau.

vi. *Brick-earths of the Darent Valley.*—These are traced along the upper course of the valley from near Limpsfield. They seem to show glacial influence, and Mr. Bell has discovered a few implements in them. The Limpsfield deposit is from 10 to 30 feet below the adjacent gravel. Brick-earth, possibly of somewhat later date, also occurs near Dartford.

vii. *Other Gravels of the Darent Valley: The Chevening and Dunton Green Drifts.*—The relations of the gravels grouped under this head are more uncertain than those of the Limpsfield stage. Various features in the gravels point to the temporary return of glacial conditions during the period of formation of these and the brick-earths: and these are described in detail.

viii. *The Low-level Valley-Gravels.*—The correlation of these is also uncertain. West of Dartford is a bed corresponding with that at Erith in which Mr. Spurrell found a palæolithic floor. It contains land- and freshwater-shells. The surface of the Chalk is here festooned under a covering of the fluviatile drift. The author attributes this festooning to the effects of cold.

ix. *The Rubble on the Sides and in the Bed of the Valley.*—The author describes this rubble, and rejects the view that it is rain-wash or due to subaerial action, and discusses the possibility of its having been produced by ice-action.

x. *Alluvium and Neolithic Implements.*—These occur chiefly between Shoreham and Riverhead.

xi. *On the Chalk Escarpment within the Darent District.*—The author, after discussing and dismissing the view that the escarpment was formed by marine denudation, criticizes the theory that it was due to ordinary subaerial denudation, and lays stress on the irregular distribution and diversity of the drift-beds in the Darent area; these do not possess the characters which we should expect if they were formed by the material left during the recession of the Chalk escarpment owing to subaerial action; and he believes that glacial agency was the great motor in developing the valleys and, as a consequence, the escarpment, and that the denudation was afterwards further carried on in the same lines by strong river-action and weathering, though supplemented at times by renewed ice-action. By such agencies, aided by the influence of rainfall and the issue of powerful springs, he considers that the escarpment was gradually pared back and brought into its present prominent relief.

February 4, 1891.—A. Geikie, Esq., LL.D., F.R.S., President, in the Chair.

The following communications were read:—

1. "The Geology of Barbados and the West Indies.—Part I. The Coral Rocks." By A. J. Jukes-Browne, Esq., F.G.S., and Professor J. B. Harrisor, M.A., F.G.S.

The authors first discuss the reef growing round Barbados and describe a submarine reef, the origin of which is considered; and it is pointed out that there is no sign of any subsidence having taken place, but every sign of very recent elevation. They then describe the raised reefs of the island, extending to a height of nearly 1100 feet above sea-level in a series of terraces. The thickness of the coral-rock in these is seldom above 200 feet, and the rock does not always consist of coral-debris. At the base of the reefs there is generally a certain thickness of detrital rock in which perfect reef-corals never occur.

The collections of fossils made by the authors have been examined by Messrs. E. A. Smith and J. W. Gregory. Of the corals, 5 out of 10 species identified still live in the Caribbean Sea, and 1 is closely allied to a known species, whilst the other 4 are only known from Prof. Duncan's descriptions of fossil Antiguan corals. The authors are of opinion that the whole of the terraces of Barbados, the so-called "marl" of Antigua, and the fossiliferous rocks of Barbuda are of Pleistocene age.

They proceed to notice the formations in other West Indian

islands which appear to be raised reefs comparable with those of Barbados, and show that these reefs occur through the whole length of the Antillean Chain, and indicate a recent elevation of at least 1300 feet, and in all probability of nearly 2000 feet. It appears improbable that each island was a region of separate uplift, and as a plateau of recent marine limestone also occurs in Yucatan, this carries the region of elevation into Central America, and it is reported that there are raised reefs in Colombia. The authors conclude that there has been contemporaneous elevation of the whole Andean Chain from Cape Horn to Tehuantepec and of the Antillean Chain from Cuba to Barbados. Before this there must have been free communication between the Atlantic and Pacific Oceans, which is confirmed by the large number of Pacific forms in the Caribbean Sea. Under such geographical conditions the great equatorial current would pass into the Pacific, and there would be no Gulf Stream in the North Atlantic.

2. "The Shap Granite, and the Associated Igneous and Metamorphic Rocks." By Alfred Harker, Esq., M.A., F.G.S., and J. E. Marr, Esq., M.A., Sec. G. S.

The authors describe the normal granite of the intrusion, and discuss the characters of certain variations from the usual type.

The dykes and sills of the neighbourhood are also considered: the similarity of some of these to certain inclusions in the granite is noticed; and reasons are given for supposing that many of the felsites and mica-traps of this region are connected with a magma which was intruded amongst the Lower Palæozoic rocks in pre-Carboniferous times, and with which the Shap granite is itself connected.

The metamorphic effects of the granite upon the surrounding rocks are then described. A remarkable set of changes produced in a series of andesites and another of rhyolites, with their respective pyroclastic rocks, is considered in detail, and the results of the metamorphism of the Coniston Limestone series and the Coniston Flags and Grits are given and compared with those obtained by other workers in Norway, the Harz Mountains, and elsewhere.

XXXIII. *Intelligence and Miscellaneous Articles.*

OBSERVATIONS ON THE PAPER BY PROF. TROWBRIDGE, "MOTIONS OF ATOMS IN THE ELECTRICAL DISCHARGE" (Phil. Mag. 5th series, vol. XXX. p. 480, 1890). BY E. WIEDEMANN AND H. EBERT.

TO the paper of Prof. Trowbridge cited above, in which he proves that the molecules in electrical discharges possess no motion of

translation in the direction of the discharge, we beg to make the following historical observations :—

1. When von Zahn investigated the spectral lines of a discharge-tube, in one case in a direction at right angles to the axis, and then in the direction of the axis itself, the lines were not displaced, although he was able to distinguish even the $\frac{1}{40}$ of the distance of the D lines. This displacement would have corresponded to a velocity of one geographical mile in the direction of the axis *.

2. Preliminary experiments of Tait, in which the spectra of a tube containing bromide of carbon were found to be the same both when parallel and at right angles to the discharge-tube, showed that the velocity must be far greater, about 90 geographical miles in a second.

3. But that it can neither attain the value obtained by von Zahn, still less a higher one, follows from the experiments of E. Wiedemann and H. Ebert †, which were obtained both by the method of Fraunhofer's minima of the second class, as well as by the method of high interferences.

4. The method employed by Prof. Trowbridge, as he himself states, shows changes in the wave-length of 1/4000 ; that used by Wiedemann and Ebert, of which, as well as of the other methods mentioned above, Professor Trowbridge makes no mention, shows a change of 1/834,000 of the value. The latter is therefore about 200 times as sensitive as the former.

Erlangen, January 1891.

ON HERTZ'S ELECTRICAL VIBRATIONS IN AIR. BY E. SARASIN AND L. DE LA RIVE.

A very thin lead plate 2·95 metres broad and 2·8 metres high, was suspended vertically. The primary conductor was horizontal, and placed either at 5·7 or 9 metres distance from the lead plate, and parallel to it ; its spark was formed in the perpendicular to the centre of the plate. The space in front of the lead plate was explored by means of a circular resonator, which was displaced along a divided scale on the normal to the lead plate. The scintilla at the break is, as observed by Hertz, stronger when the continuous part of the circuit in which the induction preponderates is in a loop, and the break is in a node, whereby for each node the break can be turned to or away from the reflecting lead plate. Close to the reflector is a node. With various primary conductors and resonators of 1, 0·75, 0·5, 0·36, 0·25, and 0·20 metre in diameter, almost the same intermediate spaces were found as along wires. The velocity of propagation through air is thus essentially the same as with wires. In this case also the resonance is a multiple one :

* Wiedemann's 'Electricity,' vol. iv. p. 580.

† Wiedemann's *Annalen*, vol. xxxvi. p. 553, 1889.

the existence of simultaneous, but different wave-lengths proceeding from the same primary conductor may be established; only in air are the limits much closer than in wires. In order to obtain clear results the dimensions of the primary conductors must here bear a given ratio to that of the resonator, which does not differ greatly from unity.

For circles of the diameter 2R, the distance of the node in air L, and in the wires D, there was obtained:—

2R	0·26 m.	0·36	0·75
L	1·12–1·25 m.	1·40–1·80	3·00–3·3
D	1·12	1·47	2·96

The waves in air are thus not at all, or but little, longer than in wires.—*Archiv. de Genève*, [3] xxii. p. 557 (1890); *Beiblätter der Physik*, vol. xiv. p. 1200 (1890).

ON THE CONDUCTION OF ELECTRICITY BY THE VAPOURS OF HEATED SALTS. BY SVANTE ARRHENIUS.

The author gives a long and important paper on this subject; the method of experimenting was to produce the vapour in the flame of a Bunsen-burner, and to measure the conductivity between two platinum wires placed at a given distance from each other. The various experimental precautions are fully described and discussed; the experiments extended to various classes of salts, and the author sums up his conclusions as follows.

The extremely fruitful hypothesis of van't Hoff, that matter in the form of gas and in that of dilute solution has perfectly analogous properties, has so far been established in the most brilliant manner; and with the aid of the laws of gases a light has been thrown on the nature of solutions, hitherto undreamed of. In the present paper I have followed the reverse way, and with a knowledge of the electrolytic properties of dilute solutions the same properties which have hitherto been unknown have been demonstrated in gases. Hence there is a complete analogy in this respect between the two conditions of matter.—Wiedemann's *Annalen*, vol. xlii. p. 18 (1891).

ELECTRICAL WAVES. BY ERNST LECHER.

The author describes a new method of studying Hertz's phenomena. Instead of a resonator of the type employed by the latter, a Geissler tube is used. Two parallel wires of known self-induction terminate at one end in condenser-plates, which are charged in an oscillatory manner by a large Ruhmkorf coil excited by storage-cells. Upon the other ends of the parallel wires rests

the Geissler tube. A short wire is then slid along the parallel wires connecting them across like a bridge between two parallel wires on a sonometer. At certain definite points the Geissler tube glows, and the wave-lengths of the electrical oscillations can thus be measured. Lecher finds that the velocity of electricity in metallic wires is the same as that of light. He points out a slight inaccuracy in Hertz's work.—*American Journal of Science*, Feb. 1891, p. 156; *Ann. der Physik*, Nov. 12, 1890, pp. 850–870.

ON THE HEAT OF EVAPORATION OF LIQUEFIED GASES.
BY E. MATHIAS.

The author uses a calorimetrical method of constant temperature; the heat withdrawn from the water-calorimeter by the evaporation of the gas is each moment restored by bringing strong sulphuric acid into the water of the calorimeter. It was therefore necessary to determine the heat of dilution of the sulphuric acid required for the measurements. With this view small glass flasks containing sulphuric acid were broken under water. A copper cylinder 3 cm. in diameter and 9 cm. in height was used as evaporator; this is connected at the top to a serpentine tube which was coiled several times round the cylinder, and on its emergence from the Berthelot's calorimeter it was insulated thermally from the rest of the tube by a connector of celluloid.

In the latter were two taps, a manometer, and finally a flask of special construction containing glycerine, in order accurately to control and regulate the rapidity of the evaporation. The introduction of the sulphuric acid was effected by an apparatus of the nature of a wash-bottle. Those parts of the metal which came in contact with the acid were thickly gilded The author worked with sulphurous acid, nitrous oxide, and especially with carbonic acid with a range of temperature of 0° to 31°. At the high temperatures the whole room was heated to the corresponding temperature.

In this way even the worst determinations did not differ by more than 2 per cent. from the mean. The results of experiments with SO_2 and CO_2 agree very well with those deduced from Clapeyron's equations. The differences with nitrous oxide arise from the gas being impure from the presence of nitrogen. With all three bodies the heat of evaporation decreases with increase of temperature within the interval in question. For sulphurous acid this is the linear equation,

$$\lambda = 91{\cdot}87 - 0{\cdot}384\,t.$$

For carbonic acid and nitrous oxide, whose critical temperatures are between 31° and 36°·4, the decrease is very steep and can be well expressed by a function of the temperature of the second degree. For carbonic acid,

$$\lambda' = 117{\cdot}303(31-t) - 0{\cdot}466(31-t)^2.$$

At the critical point the heat of evaporation is exactly null, as the tangent to the curve $\lambda = f(t)$ is here at right angles to the abscissa-axis. The author concludes from the preceding that for carbonic acid and nitrous oxide at any rate the specific heat of saturated vapour near the critical point is negative, and increases without limit with the absolute value. The observation on the specific heat of saturated vapour is further made, that this function is a maximum, and has possibly two points of inversion.—*Beiblätter der Physik*, vol. xiv. p. 1197; *Doctor thesis*, Paris, 1890.

ON THE THERMAL EXPANSION OF SOME AMALGAMS IN THE LIQUID STATE. BY C. CATTENEO.

The object of these researches has been to investigate certain amalgams, so as to ascertain whether in the case of perfect liquefaction the approximate law is verified that the metals retain their respective coefficients of expansion, and if, on the other hand, their formation was accompanied by an appreciable change of volume. Also to study these various amalgams of zinc, so as to calculate the density and the coefficient of expansion of this metal in the liquid state.

From his experiments the author thinks he can deduce the following conclusions:—

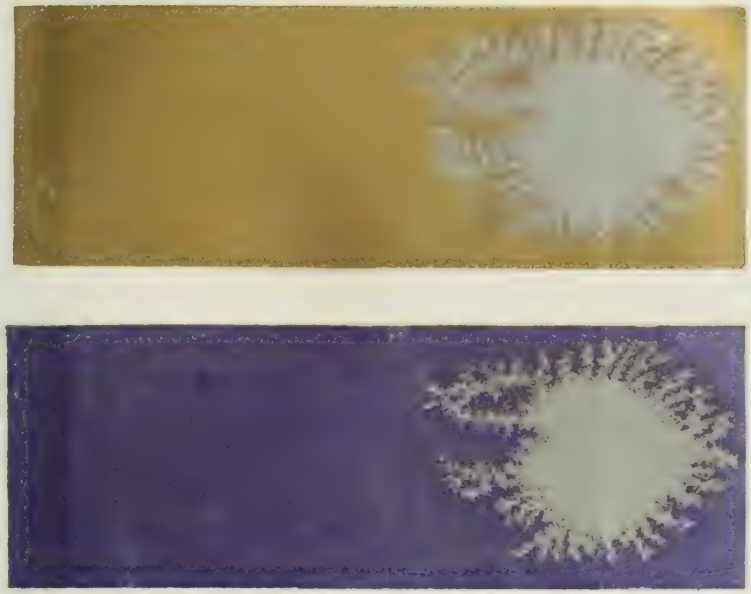
1. When the quantity of tin, of lead, or of zinc entering into the composition of an amalgam is small, the expansion of the amalgam is not equal to the sum of the expansion of the metals which form it.

2. When, on the contrary, the amalgam is dry, the comparison of the coefficients of expansion calculated from those given by experiment, show that with a sufficient approximation the metals may be regarded as retaining respectively their coefficients of expansion.

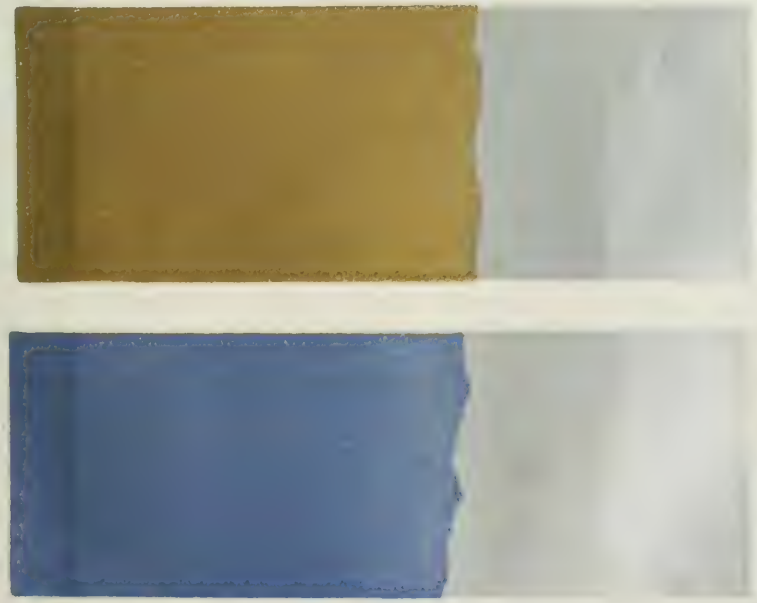
The amalgams in question have exhibited a contraction. This contraction is however, very feeble in the case of very concentrated amalgams.

The values found for the densities of tin, of lead, and of zinc in the liquid state at their respective temperatures of fusion, and for their coefficients of expansion in this same state, are sufficiently accordant with those given by Vicentini and Omodei; from which it may be concluded that, like that of alloys, the investigation of the thermal dilatation of amalgams, provided they are sufficiently concentrated, may serve to determine directly with a sufficient approximation the density and coefficient of expansion of a metal in the liquid state.—*Journal de Physique* (ii.) vol. ix. p. 519, from *Atti della R. Accademia delle Scienze di Torino*, vol. xxv. p. 492.

Effect of Electricity.



Effect of Heat.



ALLOTROPIC SILVER.

Effect of Mechanical Force

Effect of Chemical Action.

ALLOTROPIC SILVER.

Effect of Light.

ALLOTROPIC SILVER.

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1891.

XXXIV. *On* Kerr's *Magneto-optic Phenomenon in the case of Equatorial Magnetization of Iron.* *By* R. Sissingh*.

1. KERR† found in the years 1877 and 1878 that, on the reflexion from magnetized iron of light polarized in a plane parallel or perpendicular to the plane of incidence, there arises in the reflected ray, in addition to the component furnished by the metallic reflexion, another component polarized in a plane at right angles to this one. An exact explanation of this phenomenon requires the determination of the amplitude and phase of the magneto-optic component and its relation to the angle of incidence. This determination, in the case of iron magnetized parallel to the plane of incidence and to the reflecting surface, is the object of the present investigation, in which the results obtained are compared with the theory of H. A. Lorentz‡. This theory permits of a more simple explanation of the phenomenon §.

2. *Method of Observation.*—If the polarizer is perpendicular or parallel to the plane of incidence, and the analyser in a plane perpendicular to the polarizer, the reflected light after

* Translated from Wied. *Ann.* vol. xlii. p. 115 (1891), by James L. Howard.

† J. Kerr, Phil. Mag. (5) vol. iii. p. 321, 1877; (5) vol. v. p. 161 (1878).

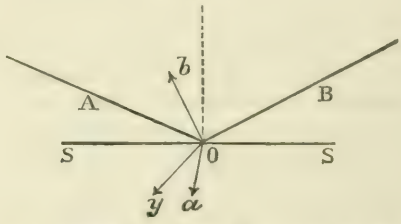
‡ H. A. Lorentz, *Verslagen en Meeded. der Acad. Amsterdam*, Reeks 2, Deel xix. (1883); *Beiblätter*, viii. p. 869 (1884).

§ For this explanation the reader may be referred to my original paper in the *Verhandelingen der Akad. von Wetenschappen* (Amsterdam), Deel xxviii.

magnetic reflexion will not be extinguished by the analyser, because the magnetic component of the light does not pass through the analyser without being weakened. By rotating one or both Nicol prisms, however, the intensity of the light can be reduced to a minimum or zero. These rotations will be called minimum- or zero-rotations, and will be designated by $\phi_{ip}^{m(o)}$, $\phi_{ia}^{m(o)}$, $\phi_{lp}^{m(o)}$, $\phi_{la}^{m(o)}$. The indices m and o denote the kind of rotation (m = minimum, o = zero), p and a indicate which Nicol prism is rotated, i and l refer to the plane of polarization of the incident light, i meaning that the light is polarized in a plane nearly parallel, and l nearly perpendicular, to the plane of incidence. Prof. van der Waals has shown how, by the help of these rotations, we can determine the amplitude μ and the phase m of the magnetic component of the light *.

For the exact determination of the quantities observed the positive direction of rotation must first be defined, and a mode of expressing differences of phase must be agreed upon. Let the observer imagine himself looking along the direction of the incident or reflected light, with his face turned towards the mirror; then the rotations of the Nicol prisms are positive if in the same direction as the motion of the hands of a watch with its face to the observer. The difference of phase of two waves of light whose oscillations are not parallel to each other is zero, if the greatest distances (of the æther molecules) from the mean position are reached at the same time for each wave. These distances, which are in a certain sense arbitrary, I have

Fig. 1.



chosen to be as given by Oy, Oa, Ob in fig. 1; Oy for incident and reflected light polarized parallel to the plane of incidence, Oa for incident and Ob for reflected light, both polarized perpendicularly to the plane of incidence. In this figure AO is the incident ray, OB the reflected ray, and SS the mirror. Oa and Ob lie in the plane of incidence; Oy is perpendicular to the plane of incidence. Oa is at right angles to OA, and Ob to OB. The differences of phase are

* *Cf.* P. C. Kaz, "*Over te terugkaatsing van het Licht door magneten*," Dissertation, Amsterdam, 1884; *Beiblätter*, ix. p. 275 (1885).

always retardations, reckoned with reference to the reflected wave polarized parallel to the plane of incidence.

In accordance with the convention adopted by all previous observers, I have called the magnetization positive if the north poles of the magnetic molecules are directed towards that side of the normal to the mirror on which the polarizer lies.

3. We can now deduce the formulæ which serve to determine the amplitude μ and the phase m of the magnetic component of the light, in the case of a bundle of incident rays polarized parallel to the plane of incidence. In these formulæ f and h are the amplitudes of the reflected light polarized parallel and perpendicularly to the plane of incidence respectively, when the incident ray has amplitude equal to unity and is polarized in the same plane. Φ is the relative difference of phase of these two waves in the case of metallic reflexion.

Let the polarizer be set parallel to the plane of incidence; and let the amplitude of the light incident on the mirror be unity. Now turn the polarizer through a small angle, ϕ_{ip}. The rays falling on the mirror are then:—

A ray polarized parallel to the plane of incidence, amplitude 1;
A ray polarized perpendicularly to the plane of incidence, amplitude ϕ_{ip}.

By reflexion, we obtain:—

A ray polarized parallel to the plane of incidence, amplitude f, retardation of phase zero;
A ray polarized perpendicularly to the plane of incidence, amplitude $h\phi_{ip}$, retardation of phase Φ; and
A ray polarized perpendicularly to the plane of incidence, amplitude μ_i, retardation of phase m_i*.

If now the analyser be turned through a small angle ϕ_{ia} out of the position in which the reflected light was quenched before the polarizer was turned and the mirror magnetized, the analyser transmits a bundle of rays with

amplitude $-f\phi_{ia}$, retardation of phase 0,
" $h\phi_{ip}$, " " Φ,
" μ_i, " " m_i.

* The indices attached to μ and m indicate that the plane of polarization of the incident ray is nearly parallel (i) or nearly perpendicular (l) to the plane of incidence.

The resulting intensity is

$$\{-f\phi_{ia}+h\phi_{ip}\cos\Phi+\mu_i\cos m_i\}^2+\{h\phi_{ip}\sin\Phi+\mu_i\sin m_i\}^2.$$

This will be a minimum when ϕ_{ia}, ϕ_{ip} have the values ϕ_{ia}^m, ϕ_{ip}^m, given by the following equations :—

$$\left.\begin{aligned}-f\phi_{ia}^m+h\phi_{ip}\cos\Phi+\mu_i\cos m_i&=0,\\ h\phi_{ip}^m-f\phi_{ia}\cos\Phi+\mu_i\cos(\Phi-m_i)&=0,\end{aligned}\right\}\quad(1)$$

These equations can also be determined by a geometrical construction for the resultant amplitude of the waves which traverse the analyser.

If the incident ray is polarized perpendicularly to the plane of incidence, we obtain in the same manner :—

$$\left.\begin{aligned}-f\phi_{lp}^m+h\phi_{la}\cos\Phi+\mu_l\cos m_l&=0,\\ h\phi_{la}^m-f\phi_{lp}\cos\Phi+\mu_l\cos(\Phi-m_l)&=0,\end{aligned}\right\}\quad(2)$$

In the above deduction quantities of the order $(\phi_{ip})^2$, $\mu\phi_{ip}$, &c. are neglected, because the rotations ϕ are only a few minutes of angle, and μ is less than 0·001*.

4. If, on reversal of the magnetization, the amplitude μ of the magnetic component of the light also changes its sign without any alteration of the phase m, it follows from the formulæ (1) and (2) that the minimum positions of the Nicol prisms are only symmetrical with respect to the plane of incidence and a plane perpendicular to it, in case the incident or reflected ray is polarized in one of these planes. ϕ_{ip}, ϕ_{ia}, ϕ_{lp}, ϕ_{la} must be equal to zero. If we call the angles between the minimum positions of the Nicol prisms for positive and negative magnetization ψ_{ip}^m &c., it follows from (1) and (2), with the above assumption :—

$$\left.\begin{aligned}\tan m_i&=-\cot\Phi-\frac{1}{\sin\Phi}\sqrt{\frac{h\psi_{ip}^m}{f\psi_{ia}^m}};\quad \mu_i=+\frac{f\psi_{ia}^m}{2\cos m_i};\\ \tan m_l&=-\cot\Phi-\frac{1}{\sin\Phi}\sqrt{\frac{h\psi_{la}^m}{f\psi_{lp}^m}};\quad \mu_l=+\frac{f\psi_{lp}^m}{2\cos m_l};\end{aligned}\right\}\quad(3)$$

* ϕ_{ip}, ϕ_{ia}, ϕ_{lp}, ϕ_{la} indicate the small angles between the plane of polarization of the Nicol prisms and the plane of incidence or a plane at right angles to it. The indices i and l mean that the incident light is polarized nearly parallel or normal to the plane of incidence. The analyser is set in a plane nearly perpendicular to the plane of incidence.

The intensity of the light emerging from the analyser after the minimum rotation ϕ_{la}^{m} is, referring back to the first formula of all, § 3,

$$(h\phi_{ip}\sin\Phi+\mu_i\sin m_i)^2.$$

If we turn the analyser out of the minimum position through an angle ϵ, the intensity alters by $f^2\epsilon^2$. As a slight alteration of intensity can be the more easily observed the smaller the original intensity, it follows that the accuracy with which the minimum rotations can be observed is greatest at small and large angles of incidence, and is smallest in the neighbourhood of the polarizing angle, where the total intensity is greatest. This accuracy is not the same for positive and negative magnetization, excepting when ϕ_{ip}, ϕ_{ia}, ϕ_{lp}, ϕ_{la} are equal to zero.

5. The positions of the Nicol prisms in which the light reflected from the magnetized mirror is extinguished by the analyser, that is the "zero rotations," are deduced from the formulæ for the intensity obtained in § 3.

These give :—

$$\left.\begin{aligned}\cot m_i &= -\frac{f\phi_{ia}^{o}}{h\phi_{ip}^{o}}\frac{1}{\sin\Phi}+\cot\Phi, \quad \mu_i=-\frac{h\phi_{ip}^{o}\sin\Phi}{\sin m_i}\\ \cot m_l &= -\frac{f\phi_{lp}^{o}}{h\phi_{la}^{o}}\frac{1}{\sin\Phi}+\cot\Phi, \quad \mu_l=-\frac{h\phi_{la}^{o}\sin\Phi}{\sin m_l}\end{aligned}\right\}\ . \quad (4)$$

If the amplitude μ, and not the phase m, of the magnetic component of the light alters its sign with the direction of magnetization, we can replace ϕ_{ia}^{o} &c. in equations (4) above by the angles ψ_{ia}^{o} . . . . , between the zero-positions of the Nicol prisms for positive and negative magnetization, these latter angles being twice as great as the former. We thus obtain a factor 2 in the numerator of the equations for μ_i and μ_l. Now it can easily be proved that the zero-rotations can be most accurately observed when $\sin\Phi$ (Φ = difference of phase on reflexion from the metal) is greatest; that is, in the vicinity of the polarizing angle. At the polarizing angle the zero and minimum rotations are equal to each other *.

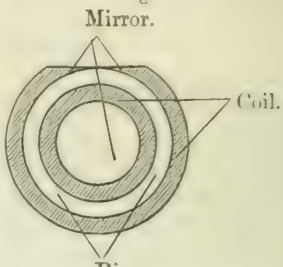
6. *Description of the Apparatus.*—The mirrors were ground on iron rings which were encircled by seven layers of windings of copper wire 1·5 to 2 millim. thick. Fig. 2 gives a

* For complete proofs of these statements the original memoir must be consulted.

section through this ring by a plane normal to the reflecting surface.

The coils do not project over the surface of the mirror. The magnetizing current was furnished by 15 Bunsen-cells, in 5 sets each containing 3 cells in parallel, the sets being joined up in series; the magnetization was measured by Rowland's method *.

Fig. 2.



In the centre of the mirror, for a magnetizing current of 15 amperes its value was 1400 C.G.S. units per unit volume. The mirror was nearly saturated; the magnetism increased 8 per cent. for a rise of current from 7·5 to 22 amperes, and only 2 per cent. between 15 and 22 amperes. These rings had the advantage that small masses of iron could be strongly magnetized, and a spectrometer used for the investigation. Two mirrors were experimented upon. The diameter of the rings was 10 centim., the thickness 0·6 centim., the length of the mirror 3 centim., and its breadth 2·8 centim.

The optical constants were determined by a Babinet's compensator †.

Mirror.	Polarizing Angle (J).	Principal Azimuth (H).
I. . . .	77° 23·5′ ‡	26° 34′
II.. . .	76° 30·5′ ‡	26° 44′

7. In the observations a parallel plane-polarized bundle of rays is reflected from the mirror, and the intensity of the reflected light is brought to zero or a minimum by rotating the analyser. In order to make measurements with very small or with normal incidence, the collimator, which gives the parallel bundle of rays, and the polarizer are separated from the spectrometer. These three parts—collimator, polarizer, and spectrometer—are so arranged that they can be moved round the edge of a circular platform.

* Rowland, Phil. Mag. (4) xlvi. p. 140, 1873.

† For the adjustment of the compensator and the method of using it, *cf.* Sissingh, Dissertation, Leyden, 1885, and *Arch. Néer.* xx. p. 171.

‡ There is a considerable difference between the polarizing-angles of the two mirrors ground and polished in the same manner. If the two mirrors were not ground and polished in exactly the same way, I often observed differences in J and H. I hope to investigate this more fully in the future.

The polarizer can be moved along a groove at right angles to this, and is inserted on a pillar provided with sights. This apparatus permits the polarizer to be rotated about a vertical or horizontal axis, and to move in a vertical direction. In this way we are able to bring the axis of the polarizer into the same line as the collimator axis, and to put the spectrometer with its axis perpendicular to this line. The rings containing the mirrors are, on account of their weight, not placed on the spectrometer table, but rest on a bridge above it. The rings can thus be rotated about a vertical axis and displaced in a horizontal direction, by means of two movable sledges at right angles to each other. This allows the centre of the mirror to be placed in the axis of the incident ray, and also permits of an exact adjustment of the mirror for all angles of incidence. For angles of incidence smaller than 24°, the analyser is also separated from the spectrometer and placed on a cross-piece which can be moved relatively to the circular platform, just as in the case of the polarizer. As the rotations to be measured only amount to a few minutes of angle, it is absolutely necessary that the different parts should be accurately adjusted and securely fastened in their proper places.

8. In order to measure accurately the small rotations, the Nicol prisms are placed in a parallel beam of light*. The collimator slit is focused by a telescope situated behind the analyser. At each point of the image of this slit we receive in this manner only those rays which pass in the same direction through the Nicol prisms, and which have therefore in these prisms the same plane of polarization. When the prisms are crossed, a dark band is observed which is displaced parallel to itself along the image of the slit on moving the polarizer or analyser. If the axes of the collimator and Nicol prisms are parallel to each other, the band occupies the centre of the image of the slit when the Nicols are crossed. All the rotations of the plane of polarization are referred to this position of the dark band. In this way we have only to adjust the position of a dark band, instead of, as in the older method, estimating when the intensity of the light is a minimum. For convenience of adjustment the centre of the slit has a fine thread stretched across it. The band is sharply defined if the intensity of the light is not too small. Further, the axes of the Nicol prisms must coincide as nearly as possible. The polarizer is a Lippich prism with plane faces which are in-

* Sissingh, Dissertation, Leyden, 1885; also *Arch. Néer.* xx. p. 178. Lippich, *Wien. Ber.* lxxxv. p. 268 (1882).

clined to each other at a small angle, viz. about 1 minute *. The tube in which the prism is fixed is attached by means of three pressure- and three tension-screws to the rim of a second tube, which is placed at the centre of the graduated circle.

Following Gauss' method, and observing the images of the telescope spider-lines reflected from the faces of the prism, the axis of the latter can be set parallel to the collimator axis. The error of this setting was less than 1′ of angle. The position of the polarizer is such that its axis coincides with that of the incident ray of light. The axis of the incident ray is found by means of a cap with a fine hole through its centre which fits over the collimator lens.

The analyser is a Nicol prism with its faces inclined to each other. The dark band was most clearly seen with such a prism. The condition for the proper position of the analyser was that the ray of light reflected from the face of the Nicol should describe a circle round the axis of the incident ray when the prism was rotated. The axis of rotation of the analyser was also made to coincide with that of the ray falling upon it.

This care in the adjustment of the Nicol prisms is absolutely necessary, in order to observe the dark band at every angle of incidence, and especially so if the angle of incidence is small. The new method of observation puts us in a position to determine small rotations with a degree of accuracy hitherto unattainable †.

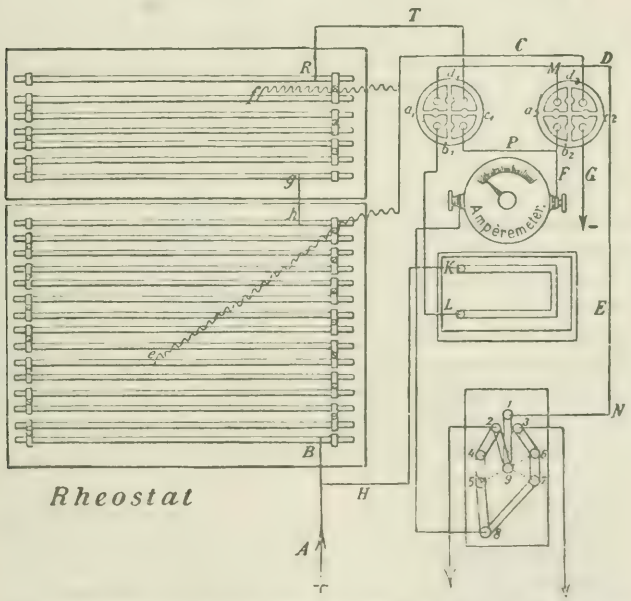
9. As the zero- and minimum-rotations only amount to a few minutes of angle in the case of magnetic equatorial reflexion, and the small circles of the Nicol prisms are divided in degrees and have no vernier, these rotations were measured by a mirror and scale method. At a distance of 2·5 metres from the polarizer were placed a telescope and scale, the former receiving the image of the scale from mirrors attached to the polarizer. These mirrors were placed on the faces of a four-sided hollow prism surrounding the polarizer-

* Lippich, *Wien. Ber.* xci. p. 1079, 1885.

† This method, which was used by me previously in the direct determination of the principal positions of Nicol prisms in which the planes of polarization are parallel and perpendicular to the plane of incidence, is now applied to the measurement of small rotations of the plane of polarization by magnetic reflexion. In this manner the principal positions are determined with a far greater accuracy than in the indirect method hitherto almost universally adopted. *Cf.* Sissingh, Dissertation, p. 28; *Arch. Néer.* xx. p. 8; Righi, *Ann. de Chim. et de Phys.* (6) iv. pp. 446, 456 (1885); ix. pp. 127–131 (1886); x. p. 208 (1887). *Cf* also § 13.

tube. The normals of the mirrors were nearly in the same plane, and made angles of nearly 90° with each other*. The polarizer was rotated by means of a long arm. In the analyser a similar arm is fixed to a ring surrounding the analyser-circle and capable of being clamped by a screw. This ring carries the mirror used in reading the rotations. Since only one scale and two telescopes, placed near together, were used for these measurements, there was added, in case the angle of incidence was not too great or too small, an auxiliary mirror, in order to permit of the analyser-rotations being measured in this manner. The scales were divided in millimetres, and 1 minute of angle corresponded to 1·4 to 1·8 millim.†

Fig. 3.



The constancy of the results obtained by this method of reading was also very satisfactory : it has been used since 1886.

10. In these experiments sunlight or electric light was used. The latter was furnished by a Siemens lamp which

* This arrangement was chosen because the polarizer is only used in the positions in which the plane of polarization is nearly parallel or perpendicular to the plane of incidence.

† In order to reduce the scale-readings to minutes, the readings are taken with the Nicols adjusted to two consecutive degrees on the divided circle.

could be displaced by the observer in a vertical direction in order to bring the crater of the positive pole always opposite the slit of the collimator.

The mirror-magnet was demagnetized by alternate currents whose absolute mean value was approximately zero. By inserting a resistance constructed out of electric-light carbons, the current could be reduced to 2·3 amperes. The ring was then inserted in a shunt-circuit, by which means the strength of the current through it could be reduced to 0·02 ampere. This arrangement was carried out by means of a switchboard, and is shown in fig. 3 with commutator, amperemeter, and two plug-switches. The key of the commutator turns round the point 9 and connects together either 1 and 2 and 6 and 7, or else 1 and 3 and 4 and 5. The magnetizing current passes from A to B, *e* (or *f*), C, plug d_2, D, E, 1, 2, ring, 3, 6, 7, 8, F, plug b_2, G. If the ring is in the shunt-circuit the main current passes along A, B, *f*, C, plug c_2, the shunt H, K, L, G, M, N, 1, 2, ring, 3, 6, 7, 8, F, P, plug c_1, T, R.

11. *Test of the Method of Observation.*—If the amplitude μ, and not the phase m, of the magnetic component of the light alters its sign with the direction of magnetization, we need not determine the angle ϕ, but only ψ (§§ 4, 5). The determination of the angle ϕ requires a knowledge of the principal positions of the Nicol prisms, in which the planes of polarization are parallel or perpendicular to the plane of incidence. This would always necessitate a demagnetization of the mirror on account of permanent magnetism. First of all we shall show that on demagnetizing, as in § 10, the principal positions of the Nicol prisms are the same, whatever sign the smallest magnetizing current of 0·02 ampere may have. The permanent magnetism therefore exerts no influence on the reflexion.

Demagnetization by Currents in alternate directions of +15 amp. to +0·02 amp.		The Mirror demagnetized afresh. Alternate Currents of +15 amp. to −0·02 amp.	
Principal positions of the		Principal positions of the	
Polarizer.	Analyser.	Polarizer.	Analyser.
144·7	304·0	144·9	304·9
143·8	304·7	144·5	303·3
144·0	303·9	144·9	305·8
145·1	304·0	145·2	304·8
145·0	305·3	144·5	303·9
145·3	305·1	144·7	303·8
145·0	304·5	145·4	304·4
145·1	303·8	144·7	303·8
144·75	304·4	144·8	304·3

The value of a minute of angle is 1·56 scale-division for the polarizer and 1·66 for the analyser*.

After the first demagnetization the Nicol prisms were left in their last position. On repeating the process of demagnetization, for the second experiment, it was seen that the dark band had not changed its position. This, together with the agreement of the mean values of the scale-readings, proves that the demagnetization was fully accomplished by the method adopted. The results of a few other sets of experiments were as follows:—

Demagnetizing Current to	Principal Positions.		Minimum Positions.	
	Polarizer.	Analyser.	Polarizer.	Analyser.
+0·02 amp.	144·75	304·4	.....	.....
−0·02 „	144·8	304·3	.....	.....
+2·3 „	.....	.....	142·5	308·0
−2·3 „	.....	.....	147·3	300·5
+0·02 „	145·0	304·5	.....	.....

These results verify the above conclusion. By a demagnetization stopping at 2·3 amperes the minimum rotations of the polarizer on account of permanent magnetism were −2·3 and +2·45, of the analyser +3·6, −3·9; or, expressed in minutes, −1′·5 and 1′·6, +2′·2 and −2′·3.

These observations were made with an angle of incidence of 51° 22′, because at this angle the minimum rotations can be observed with greater accuracy (*cf.* § 4), while the influence of permanent magnetism is not too small, its effect being a maximum for an angle of incidence of between 60° and 70° (see § 16).

12. A second proof of the full demagnetization of the mirror is furnished by the agreement between the principal positions of the Nicol prisms obtained with the demagnetized mirror and with a silver mirror respectively. The two observations must be made immediately following each other. The table of the spectrometer carrying the silver mirror comes in the place of the bridge above the spectrometer and carrying the iron mirror. However great be the care taken in this operation to keep the mirror in the proper position, the adjustment and centering of the mirror have always to be tested, and if necessary a new adjustment must be made. In place

* In the remainder of the paper these will be denoted by $1_p' = 1{\cdot}56$, $1_a' = 1{\cdot}66$.

of the analyser we have then the telescope of the spectrometer. Sometimes the polarizer was also removed, because the deviation of the light, although very small (1′), hinders the proper centering and adjustment of the mirror. It is not easy in these operations to avoid every alteration of the mirrors used to read off the rotations.

The observations gave, for the principal positions of the Nicol prisms:—

With Demagnetized Iron Mirror.	
Polarizer.	Analyser.
388·8	279·9
387·0	280·2
389·4	281·4
388·4	280·5

With the Silver Mirror.	
Polarizer.	Analyser.
388·1	279·2
388·4	282·2
388·25	280·7*

A second series of observations, in which the scale-readings were not quite the same, gave†:—

Iron Mirror demagnetized.	
Polarizer.	Analyser.
387·3	283·7
388·0	283·3
387·6	283·5

Silver Mirror.	
Polarizer.	Analyser.
387·2	284·6
387·4	283·6
387·2	283·3
387·3	283·8

Since in these observations $1_p' = 1{\cdot}33$, $1_a' = 1{\cdot}23$, we may, taking into consideration the difficulties in the experiment, conclude that the principal positions of the Nicol prisms are the same for the silver mirror and the demagnetized iron mirror.

13. Now that we have established that the demagnetization is complete, we may proceed to show that the amplitude μ of the magnetic component changes its sign with the direction of magnetization, but that the phase m is not changed by this means. From formulæ (1) and (2), § 3, and (4), § 5, it is shown that this is the case if the minimum- and zero-rotations for positive and negative magnetization differ from each other only in their sign and not in absolute value.

For an angle of incidence of 51° 22′ the minimum rotations were determined both for positive and negative magnetization —that is to say, after each series of observations with any given direction of magnetization a demagnetization of the mirror took place. An exact determination of the minimum rotations, however, required the collimator-slit to be reduced by a cross slit to a very short length. If this was not done

* Each of these numbers is the mean of 8 settings.

† As the absolute value of the scale-divisions does not influence these results, no notice was taken of its alteration.

it was always observed, on rotating the polarizer or analyser in order to again obtain a minimum intensity of light in the centre of the field of the analyser (that is, the centre of the image of the slit), after magnetizing the mirror, that the greatest minimum was not in the centre of the field but somewhat above or below this position. This minimum rendered an exact adjustment, so that the intensity of light was least in the centre of the field, almost impossible ; and therefore by means of the cross slit only the centre of the collimator-slit was left.

The minimum rotations ϕ_i^m and ϕ_l^m were determined for the two positions in which the polarizer was parallel and perpendicular respectively to the plane of incidence ; and for each position of the polarizer the analyser was read in two positions 180° apart.

The following series of observations is given in order to show what degree of accuracy is obtained ; then follow the means from several series of observations :—

Polarizer perpendicular to the Plane of Incidence.

Mirror demagnetized.		Mirror again demagnetized.	
Polarizer perpendicular to Plane of Incidence.	Analyser parallel to Plane of Incidence.	Polarizer perpendicular to Plane of Incidence.	Analyser parallel to Plane of Incidence.
385·5	281·7	385·6	283·0
385·5	282·1	386·2	283·1
386·0	282·1	386·8	283·5
386·0	283·2	386·4	283·7
385·8	283·3	386·6	284·2
385·5	282·8	385·7	282·7
385·7	282·7	386·7	283·7
385·5	282·6	385·7	283·0
385·7	282·6	386·2	283·3

Mean of these Observations.

Polarizer perpendicular to Plane of Incidence, 385·9.
Analyser parallel to Plane of Incidence, 283·0.

Polarizer perpendicular to Plane of Incidence. Minimum positions of the Analyser for Magnetization		Analyser parallel to Plane of Incidence. Minimum positions of the Polarizer for Magnetization	
+	−	+	−
278·0	288·2	382·4	389·6
277·6	288·1	381·8	389·4
278·8	288·8	381·9	390·4
278·1	289·2	382·0	390·1
278·1	288·6	382·0	389·9

It follows from these that

$$\phi^m_{la} \text{ for } + \text{ magnetization } = -1{\cdot}9,$$
$$\phi^m_{la} \text{ ,, } - \text{ ,, } = +5{\cdot}6,$$
$$\phi^m_{lp} \text{ ,, } + \text{ ,, } = -3{\cdot}9,$$
$$\phi^m_{lp} \text{ ,, } - \text{ ,, } = +3{\cdot}9.$$

The mirror was then demagnetized again, and the observations gave :—For polarizer perpendicular to plane of incidence, 385·8 ; analyser parallel to plane of incidence, 283·5. These numbers agree exactly with those obtained above.

The mean values of the rotations for positive and negative magnetization are :—

ϕ^m_{lp}.		ϕ^m_{la}.		ϕ^m_{lp}.		ϕ^m_{la}.	
Magn. +	Magn. −	Magn. +	Magn. −	Magn. +	Magn. −	Magn. +	Magn. −
+5·2	−4·2	+3·6	−4·0	−3·9	+3·95	−4·9	+5·6
5·3	5·3	3·7	3·5	4·5	3·75	4·6	4·6
5·5	4·9	3·9	3·7	4·6	3·4	5·3	5·1
4·7	5·6	4·5	4·5	3·4	4·4	5·4	5·0
+5·2	−5·0	+3·9	−3·9	−4·1	+3·9	−5·0	+5·1

As the scale-divisions were $1_p' = +1{\cdot}30$, $1_a' = -1{\cdot}27$, we obtain, on reducing these minimum rotations to minutes of angle:—

ϕ^m_{lp}.		ϕ^m_{la}.		ϕ^m_{lp}.		ϕ^m_{la}.	
Magn. +	Magn. −	Magn. +	Magn. −	Magn. +	Magn. −	Magn. +	Magn. −
+4·0	−3·8	−3·1	+3·1	−3·2	−3·0	+4·0	−4·0

On looking over the whole series of observations it was seen that the deviations from the mean value amounted in each set to about $\frac{1}{3}'$; so that the final mean values will have a slightly greater accuracy than this. Within the limits of error the

values of the minimum rotation agree for positive and negative magnetization. The mean error in the principal positions of the Nicol prisms in which the planes of polarization are parallel and perpendicular respectively to the plane of incidence has about the same value. As already previously indicated in § 8, this direct method of determining the principal positions gives far more accurate results than the indirect methods usually employed hitherto.

14. Since we may obtain the amplitude μ and the phase m of the magneto-optic component both from the minimum-rotations and the zero-rotations, we must now show that the results agree. For this purpose the zero-rotations were also determined for an angle of incidence of 51° 22′, because with large and small angles of incidence the accuracy of the observations is considerably decreased, and the minimum-rotations, which are then capable of being determined with the greatest approach to accuracy, are still sufficiently well defined. As we have already shown that only the amplitude μ and not the phase m of the magnetic component of the light changes its sign with the direction of magnetization, we only require to measure the angle ψ between the zero-positions of the Nicol prisms for positive and negative magnetization (*cf.* § 5). In the following tables the values of μ and m are given for positive magnetization. The observed rotations were :—

$2\phi^{o}_{ip}$.	$2\phi^{o}_{ia}$.	$2\phi^{o}_{lp}$.		$2\phi^{o}_{la}$.	
−0′·3	−6′·4	−6′·6	−6′·75	−0′·4	−0′·4
		−6′·9		−0′·4	
−0′·6	−7′·3		−6′·9		−0′·3
−0′·45	−6′·85		−6′·8		−0′·35

A discussion of the different series of observations shows that the mean error in these numbers is smaller than 0′·5. From the minimum- and zero-rotations the following values of μ and m were obtained† :—

$2\phi^{o}_{p}$.	$2\phi^{o}_{ia}$.	$2\phi^{o}_{lp}$.	$2\phi^{o}_{la}$.	μ_i.	μ_l.	m_i.	m_l.
·4	−6′·8	−6′·8	−0′·3	$+0{\cdot}79\times10^{-3}$	$+0{\cdot}81\times10^{-3}$	180°−1° 9′	180°−0° 52′
·2*	−6′·6*	−6′·8*	−0′·5*	+0·69* ,,	+0·78* ,,	180°−3° 40′*	180°−1° 17′·5*
$2\phi^{m}_{p}$.	$2\phi^{m}_{ia}$.	$2\phi^{m}_{lp}$.	$2\phi^{m}_{la}$.				
·9	−6′·2	−6′·8	8′·0	0·754 ,,	0·756 ,,	180°+5° 35′	180°+7° 21′
·8*	−6′·2*	−6′·4*	7′·8	0·750* ,,	0·765 ,,	180°+3° 47′*	180°+0° 37′

† The formulæ (3) and (4), § 4 and § 5, leave the sign of the amplitude μ undetermined, and the quadrant in which the phase m lies depends upon this. In the table μ_i and μ_l are always taken as positive.

In order to determine the influence of a small alteration in the observed quantities upon the calculated numbers, the values of μ and m were reckoned for the rotations denoted by an asterisk and chosen at random. From the observations and the calculated values, we may conclude that

$$\phi_{ip} = \phi_{la}, \quad \phi_{lp} = \phi_{ia},$$

either for zero- or minimum-rotations, and also that

$$\mu_i = \mu_l, \quad m_i = m_l.$$

Two of the zero-rotations, ϕ^o_{ip} and ϕ^o_{la}, are nearly equal to zero for this angle of incidence. The light reflected from the magnetized mirror can therefore be extinguished by a rotation of one of the two Nicol prisms. The influence of the magnetization is at this angle of incidence almost equivalent to a rotation of the plane of polarization. The other two zero-rotations, ϕ^o_{ia} and ϕ^o_{lp}, must therefore differ but slightly from the corresponding minimum-rotations, which is the case.

It is clear from the tabulated observations that, within the limits of error, the minimum- and zero-rotations give the same results. The degree of accuracy of the amplitudes μ reckoned from ϕ^m, and of the phases m reckoned from ϕ^o, is fairly high. The error is not greater than 1 per cent.

15. In the observations one has to be very careful that the reflexion takes place exactly at the centre of the mirror, since the magnetic spectrum showed that only in this position are the lines of force parallel to the reflecting surface. If by means of an auxiliary reflector, inclined at an angle of 45° to the normal to the mirror, we allowed the light to fall perpendicularly on the mirror, the magnetization always produced some effect unless the reflexion took place exactly at the centre of the mirror. This can only arise from the component of magnetization normal to the mirror. However small was the inclination to the mirror of the lines of force outside its centre, the sign of the magnetization could always be determined by the displacement of the band in the field of the analyser. In order to eliminate entirely the influence of a normal component of the magnetization, the section of the incident pencil of light was reduced to a few square centimetres.

16. *Synopsis of Results. Comparison with Theory.*—The zero- and minimum-rotations were determined for various angles of incidence with both mirrors. These angles of incidence were so chosen that the difference in phase of the metallic reflexion varied from one to the next by $\frac{1}{16}$ of a wave-length, except for angles less than 36°, when the differences were $\frac{1}{2}$ wave-lengths. The angle of incidence 61° 30′ was chosen in order to more accurately determine the maximum value of the amplitude μ. The observed and calculated quantities are collected in the following Table :—

Magnetic Reflexion.—Lines of Force parallel to the reflecting surface.
Magnetization per unit volume = 1400 C.G.S. units.

Mirror I. J = 77° 23′·5 ; H = 26° 34′.
„ II. J = 76° 30′·5 ; H = 26° 44′. Yellow light.

Angle of Incidence.	Mirror.	Kind of Adjustment. o = zero. m = min.	Observed Rotations. $2\phi_{ip}$.	$2\phi_{ia}$.	$2\phi_{lp}$.	$2\phi_{la}$.	$10^3 \times \mu_i$.	$10^3 \times \mu_l$.	$m_i - 180°$.	$m_l - 180°$.
° ′									° ′	° ′
86 0	II.	m	−1·8	−1·7	−1·7	−1·8	+0·28	+0·28	29 26	29 26
82 30	II.	o	4·0	−4·9	−5·0	−3·7	0·50	0·56	25 39	23 4·5
76 30·5	II.	o	2·7	−5·2	−4·8	2·6	0·74	0·69	14 23	15 14
71 25	II.	o	2·2	−5·9	−5·2	2·2	0·86	0·77	9 29	10 37
61 30	I.	o	−0·4	−5·9	−6·3	−0·2	0·81	0·83	2 22	1 6
51 22	I.	o	−0·9	−6·8	−6·5	−0·3	0·75	0·77	2 24	−0 44
	I.	o	−0·2	−6·8	−7·0	−0·6	0·82	0·80	−0 35	−1 25
	II.	o	−0·4	−6·8	−6·8	−0·3	0·79	0·81	−1 9	−0 52
	II.	m	7·9	−6·2	−6·2	−8·0	0·75	0·75	[5 35	7 21]
	I.	m	8·0	−6·5	−6·5	8·2	0·79	0·80	[1 15	5 5]
36 10	II.	o	−3·7	−8·9	−8·5	−3·8	0·66	0·60	5 31	6 11
	I.	o	.....	.....	−6·9	−3·0	.....	0·50	...	5 33
	I.	m	6·1	−5·7	−5·6	6·3	0·68	0·66	[14 7	2 59]
24 16·5	II.	m	3·9	−3·7	−3·8	3·9	0·41	0·45		
			3·9*	−4·0	.....	.....	0·61*			
12 0	I.	m	2·0	−1·9	−1·9	2·0	0·26	0·26		
			.....	.....	−2·0*	2·1	.....	0·54*		
6 0	II.	m	1·0	−1·0	−0·96	−0·96	0·14	0·11		
			1·0*	−0·997*	.....	.....	0·10*			
			1·0*	−0·95*	.....	.....	1·18*			

The numbers marked with an asterisk are values chosen at random, and serve to show the influence of a small alteration in the observed rotations upon the calculated amplitudes and phases of the magnetic component of the light. A glance at the Table will show that the mean error in μ is $0{\cdot}03 \times 10^{-3}$, and in m about 1°. For angles of incidence smaller than 51°, the relative error in the phases m obtained from the values of ϕ^m is great; while for $i=24°$ or smaller, a small alteration in the differences of ϕ^m_{ip} and ϕ^m_{ia}, or ϕ^m_{lp} and ϕ^m_{la} alters the amplitude μ very considerably.

The results obtained show that, within the limits of experimental error, $\phi^{m \text{ or } o}_{ip}=\phi^{m \text{ or } o}_{la}$, and $\phi^{m \text{ or } o}_{lp}=\phi^{m \text{ or } o}_{ia}$. It follows from these relations that $\mu_i=\mu_l$; $m_i=m_l$. All previous observers have found the same result. We must, however, have regard to the assumptions with respect to signs made in order to completely specify μ and m*.

In the neighbourhood of the angle of incidence $i=60°$, the zero-rotations ϕ^o_{ip} and ϕ^o_{ia} are equal to zero. The magnetization then produces only a rotation of the plane of polarization. For an angle of incidence of about 80° the minimum-rotations are zero, *i. e.* $\phi^m_{ip}=\phi^m_{la}=0$. The reversal of sign of these rotations can be seen in the Table, since at the principal angle of incidence J = 76° 30′·5, the minimum- and zero-rotations are equal to each other. For this angle of incidence, there is a difference of 90° in the retardations of phase of the magneto-optic component and that component of the metallic reflexion which is polarized perpendicularly to the plane of incidence.

If a pencil of light polarized parallel to the plane of incidence falls on a magnetized iron mirror, the reflected light is in general elliptically polarized, but in the neighbourhood of $i=60°$ it is plane-polarized. If the incident ray is polarized perpendicularly to the plane of incidence, we have at $i=80°$ the peculiarity that the axes of the ellipse which represent the paths of the æther molecules, are parallel and perpendicular respectively to the plane of incidence†.

* Righi found, for example, that $\phi^m_{ip}=-\phi^m_{la}$; $\phi^m_{ia}=-\phi^m_{lp}$. By an alteration of the direction which we have called the positive direction of rotation of one of the Nicol prisms, we can make the signs agree with our results.

† Righi, *Ann. de Chim. et de Phys.* (6) x. pp. 212, 219 (1887) assumes that the influence of magnetization consists in producing a rotation of the plane of polarization together with ellipticity of the reflected light. For an angle of incidence $i=60°$, the ellipticity is zero, and for $i=80°$ the rotation is zero. Righi calls the first angle "incidence singulière," and the second, the principal angle of incidence of magnetized iron. From the observations given above, it is obvious that this can only apply to a particular plane of polarization of the incident light.

17. Prof. H. A. Lorentz has shown how the Hall phenomenon leads to an explanation of magnetic reflexion, if we assume that every movement of electricity in a magnetic field is accompanied by a transverse electromotive force. In this theory it is assumed that the constant of magnetic polarization is the same for air and iron; that is to say, the magnetic iron molecules cannot direct themselves in accordance with the rapidly alternating magnetic forces of visible electric vibrations (light). I have put forward an experimental proof of this, inasmuch as it has been shown that reflexion from iron does not differ in the least from reflexion at the surface of a non-magnetic metal*. The theory further considers the behaviour of ordinary electric currents and of visible electric vibrations to be the same. This, however, has not yet been experimentally proved. But I have not been able to detect any difference in the constants of reflexion of iron at 120° C., and at ordinary temperatures, although the fairly large influence of temperature on electrical resistance would lead us to expect such a result according to this theory †.

It is, however, very important to compare the results of observation with theory. In this way we obtain experimental indications of the behaviour of visible electric vibrations in metals ‡.

If we have regard to the difference between the positive direction of vibration, which we have assumed in order to completely specify the phase-differences, and that which is derived from theoretical investigations, we find from the electromagnetic theory of magnetic reflexion § that

$$\mu_i = \mu_l = \frac{\sigma^3 \sin\alpha}{\rho_1 l'^2_1 l'_4 \cos^3\alpha} \cdot \frac{2\pi}{T} \epsilon_1 h \mathrm{N}.$$

$$m_i = m_l = 3\tau - \omega - \frac{\pi}{2} - 2\delta_1 - \delta_4 - (\delta_2 - \delta_1).$$

α is the angle of incidence, σ, ρ, τ, ω are auxiliary quan-

* Sissingh, Dissertation, p. 129; also *Arch. Néer.* xx. p. 213 (1886).

† Sissingh, *loc. cit.* p. 133; *loc. cit.* p. 215 (1886).

‡ Sissingh, *loc. cit.* p. 139; *loc. cit.* p. 218 (1886). Kundt has questioned the accuracy of the above conclusion. It is, however, borne out by the small influence of temperature which Du Bois found in the case of normal polar magnetic reflexion (Wied. *Ann.* xxxix. p. 35, 1890).

§ H. A. Lorentz, *Versl. en Meded. der Acad. Amsterdam*, Reeks 2, Deel xix. (1883); van Loghem, *Theorie der terugkaatsing van het Licht door magneten*, Leyden, 1883, Dissertation; also *Beibl.* viii. p. 869 (1884).

tities from the theory of metallic reflexion*. The remaining quantities are determined by the equations :—

$$\tan \delta_1 = \frac{m \sin (\tau + \omega)}{1 + m \cos (\tau + \omega)},$$

$$\tan \delta_2 = \frac{m \sin (\tau + \omega)}{-1 + m \cos (\tau + \omega)},$$

$$\tan \delta_4 = \frac{m \sin (\tau + \omega)}{\tan^2 \alpha + m \cos (\tau + \omega)}.$$

$$p_1^2 = 1 + m^2 + 2m \cos (\tau + \omega),$$

$$p_4^2 = \tan^4 \alpha + m^2 + 2 \tan^2 \alpha \, . \, m \cos (\tau + \omega),$$

$$m = \frac{\sigma \rho}{\cos \alpha} \dagger.$$

From these formulæ μ and m have been calculated for different angles of incidence. The theoretical value of the amplitude contains the factor $\frac{2\pi}{T} \epsilon_1 h N$, in which N is the magnetic force, T the time of oscillation of the electrical wave-motion (the incident light-wave), ϵ_1 is the constant of dielectric polarization of air, and h is the magnitude of the Hall transverse electromotive force. This latter is equal to hN times the component of the electric current by which it is produced, in consequence of the magnetic force N. On account of the unknown quantity ϵ_1, this factor, which in the remainder of the paper we shall call A, cannot be calculated. Therefore, instead of the theoretical amplitudes, only numbers proportional to them have been calculated. In the following Table only the means of μ_i and μ_l, m_i and m_l are given, since we have already shown (§ 16) that these quantities are equal to each other within the limits of error.

* *Cf.* § 19.

† A discussion of the theoretical considerations will give the signs of the quantities involved in these formulæ and the quadrants to which τ, ω, and the various δ's belong. Cf. *Verhandel. Acad. Amsterdam*, Deel xxviii. (1890).

Equatorial Magnetization per unit volume = 1400 C.G.S. units.

Mirror I. $J = 77° 23'·5$; $H = 26° 34'$.
„ II. $J = 76° 30'·5$; $H = 26° 44'$. Yellow light.

Mirror.	Angle of Incidence.	Amplitude of the Magnetic Component of Light.		Obs. Ampl. / Calc. Ampl. $\times \frac{10^{-3}}{A}$.	Phase of the Magnetic Component of Light.		Observed − Calculated Phase.
		Calc. $\times A$.	Obs. $\times 10^{-3}$.		Calc.	Obs.	
						180°	180°
II.	86° 0′	0·226	0·284	1·26	−54° 16′·5	+29° 26′	+83° 42′·5
II.	82 30	0·358	0·530	1·48	−62 22	+24 22	+86 44
II.	76 30·5	0·493	0·715	1·45	−69 51·5	+14 49	+84 40·5
II.	71 52	0·548	0·815	1·48	−73 44·5	+10 3	+83 47·5
I.	61 30	0·598	0·820	1·37	−81 36·5	+ 1 49	+83 35·5
II.	51 22	0·545	0·760	1·39	−85 55	− 1 0	+86 55
II.	36 10	0·426	0·630	1·48	−90 1·5	− 5 51	+84 49
II.	24 16·5	0·266	0·430	1·62	−91 56		
II.	12 0	0·152	0·260	1·69	−93 2·5		
II.	6 0	0·074	0·125	1·69	−93 1·5		

Since in the factor A, Hall's constant h for iron is positive, and since this depends upon the choice of the system of coordinates, and the positive directions of the magnetic force N in these observations and in the theory of magnetic reflexion are opposite to each other, the signs of the calculated and observed amplitudes do not agree with each other, because they are both referred to positive magnetization. The sign of the amplitude of a wave-motion can, however, be changed by making the phase 180° large or smaller. In the rest of the paper the phases have been so changed in order to give the amplitudes the proper signs. The differences given in the last column will then be 180° greater or smaller.

The observations showed that $\mu_i = \mu_l$; $m_i = m_l$. This relation follows also from theory. As we can only write down proportional values for the theoretical amplitudes, the observed and calculated amplitudes agree with each other within the limits of experimental error. But there is a constant difference between the observed and calculated phases. The deviations from the mean value lie within the limits of error.

Perhaps this difference of nearly 90° points to a difference in the behaviour of ordinary electric currents and the periodic motions of the electric theory of light. As we have already seen, this can be shown by other methods *.

18. Kerr, who discovered the influence of magnetization on reflexion at the surface of iron, gives only the sign, and not the magnitude, of minimum-rotations. His results agree with my observations. In his case, too, there was a change of sign at an angle slightly greater than the principal angle of incidence. Kerr found a maximum of the minimum-rotation in the neighbourhood of 60°. In my observations the maximum amplitude of the magnetic component of the light was reached between 60° and 70°, but the maxima of rotation and amplitude do not coincide. It is worthy of note that Kerr has also used the motion of the dark band in the field of the analyser as the most accurate means of adjustment. With respect to the phase of the magneto-optic component, Kerr mentions that it approximates more nearly to zero than to 90° in the case of angles of incidence less than the principal angle. According to my observations, this is the case for every angle of incidence for which the phase can be accurately determined.

The signs and magnitudes of the minimum-rotations of the analyser given by Kundt † agree with mine, with the exception of some slight differences of magnitude.

Righi's investigation ‡ appeared in the year 1887, after I had commenced these measurements. I have calculated the amplitudes and phases of the magnetic component of the light from the numerous angles of incidence given by Righi (Table opposite). The principal angle of incidence and azimuth were assumed the same as that for my mirror No. II.

Where two values of μ and m are given for the same angle of incidence, the first values are calculated from the minimum- and the second from the zero-rotations. We cannot conclude from these observations that the observed and calculated amplitudes are proportional to each other, much less that the difference between the calculated and observed phases is constant. The rotations must be measured with greater accuracy before we can draw the conclusion. To reach this degree of accuracy it is absolutely necessary to test the method of observation. The influence of errors of observation masks these relations. Since Righi did not calculate ary

* Although the theory of magnetic reflexion which Fitzgerald has given really applies only to transparent media, yet the amplitudes reckoned from it are also proportional to the observed values.

† Kundt, Wied. *Ann.* xxiii. p. 244 (1884).

‡ Righi, *Ann. de Chim. et de Phys.* (6) x. p. 200 (1887).

The Amplitudes μ and Phases m calculated from Righi's Observations.

Angle of incidence.	$2\phi^{m}_{ip}$.	$2\phi^{m}_{ia}$.	$2\phi^{m}_{lp}$.	$2\phi^{m}_{la}$.	$2\phi^{o}_{ip}$.	$2\phi^{o}_{ia}$.	$2\phi^{o}_{la}$.	$2\phi^{o}_{lp}$.	$10^{3}\mu_{i}$.	$10^{3}\mu_{l}$.	m_{i}.	m_{l}.	$\frac{\mu obs.}{calc.}$	$m$obs. $-$ $m$calc.
											180°	180°		
85 0	−3·0	−3·0	−3·0	−3·0	.....	.....	.....	.....	0·48	0·48	+29° 26′	+29° 26′	1·78	85° 58′·5
82 0	.....	.....	.....	.....	4·5	−4·5	−5·5	4·0	0·31	0·26	+64 10	+67 30	0·77	128 49·5
80 0	.....	.....	−6·0	−1·0	.....	.....	.....	.....	.....	0·87	.....	−17 2	2·04	82 35·0
78 54	0	−6·7	−6·7	0	5·0	−6·5	−6·5	4·5	0·95	0·90	−14 46	−14 46	2·07	81 39·0
									−0·53	−0·41	−40 18	−48 22	1·05	111 13·0
75 0	.....	.....	−7·0	4·5	.....	.....	.....	.....	.....	0·96	.....	−10 22	1·87	90 9·0
70 0	6·7	−7·9	−8·0	6·5	.....	.....	.....	.....	1·04	1·05	− 2 36	− 3 53	1·90	75 48·5
60 0	11	−9·0	−9·0	11	−2·0	−9·0	−8·7	−1·3	1·13	1·13	− 1 33	− 1 33	1·90	83 37·0
									1·17	1·18	− 5 24	− 3 29	1·97	86 33·0
50 0	10	−9·0	−9·0	11	−6·0	−13	−13	−6	2·81	2·58	−67 20	−67 20	5·08	9 8·5
									2·00	2·00	−10 38	−10 38	3·70	75 45·0
40 0	7·9	−6·7	−7·0	8·0	.....	.... .	.....	.....	0·78	0·81	7 6	− 1 14	1·74	95 35·0
30 0	6·6	−6·6	−7·0	7·6	.....	.....	.....	.....	0·90	1·01	−34 19	−45 50	2·63	51 31·5
20 0	4·0	−5·0	−5·0	4·0	.....	.....	.....	.....	2·64	2·64	−77 57	−77 57	1·03	.....
10 0	2·5	−2·5	−2·7	2·3	.....	.....	.....	.....	0·34	3·00	−37 43	90°−5° 36′	2·47	.....

amplitudes or phases he attaches more weight to the rotations themselves, and determines fully the changes of sign. Moreover, the principal angle of incidence of magnetized iron and the singular angle of incidence are introduced. These hold good, as we have already seen in § 16, only for one particular plane of polarization of the incident light.

19. The observations recorded in this paper furnish an accurate representation of magnetic reflexion, which, on comparison with theory, assumes a simple form. In order to demonstrate this clearly, I have given a table of the constant quantities, and the relations between these and the observed quantities, which suffice to fully determine metallic and magnetic reflexion.

Ordinary Metallic Reflexion.

Jamin's Constants :—

J = Principal Angle of Incidence.
H = Principal Azimuth.

Magnetic Reflexion.

Constants of Equatorial Reflexion :—

$\Theta = 1{\cdot}5 \times 10^{-3}$; $S = 85°$*.

Quantities used in presenting the Theories :—

Φ = Difference of phase between the light polarized parallel and and perpendicular to the plane of incidence.

f = Amplitude of the reflected component, polarized parallel to the plane of incidence.

h = Amplitude of the reflected component, polarized perpendicularly to the plane of incidence.

Cauchy's Formulæ for calculating the ratios of amplitudes and the differences of phase for an angle of incidence α :—

$$\tan \Phi = \sin(\tau+\omega) \tan \left\{ 2 \arctan \frac{\sin^2 \alpha}{\sigma\rho \cos \alpha} \right\} \cos \left\{ 2 \arctan \frac{h}{f} \right\}$$

$$= \cos(\tau+\omega) \sin \left\{ 2 \arctan \frac{\sin^2 \alpha}{\sigma\rho \cos \alpha} \right\}.$$

Δ = Phase of the magnetic component of the light.

μ = Amplitude of the magnetic component of the light.

Formula for calculating the amplitude, the form of which is borrowed from theory :—

$$\mu_i = \mu_l = \frac{\sigma^3 \sin \alpha}{\rho p_1 \mu_1 \cos^3 \alpha} \Theta.$$

Formula for calculating the difference of phase : —

$$\Delta = \Delta_0 + S.$$

$$\Delta_0 = 3\tau - w + \frac{\pi}{2} - 2\delta_1 - \delta_4 - (\delta_2 - \delta_1).$$

---

* Θ is the ratio of the observed to the calculated amplitude, and S is the constant difference between the observed and calculated phases.

Auxiliary Quantities determined by J and H:—

σ, τ*.

Auxiliary Quantities determined by J, H, α:—

ρ, ω †.

Observed Quantities:—

Φ, $\frac{h}{f}$ = Azimuth of the polarization produced.

Auxiliary Quantities determined by J, H, α:—

$\bar{c}_1$, $\bar{c}_2$, $\bar{c}_4$, p_1, p_4 ‡.

Observed Quantities:—

$\phi_{ip}^{m(o)}$, $\phi_{ia}^{m(o)}$, $\phi_{lp}^{m(o)}$, $\phi_{la}^{m(o)}$.

Relations between the observed and calculated values:—See §§ 4, 5.

---

* σ and τ are determined by

$$2\mathrm{H}=\tau+\omega\,;\quad -\cos 2\mathrm{J}=\frac{\tan(\tau-\omega_3)}{\tan(\tau+\omega_3)}\,;\quad \rho=\tan\mathrm{J}\sqrt{\frac{\cos 2\mathrm{H}}{\cos(\tau-\omega_3)}}.$$

† ρ and ω are determined by

$$\cot 2\omega=\frac{\sigma^2}{\sin^2\alpha\sin 2\tau}-\cot 2\tau\,;\quad \rho^2\sin 2\omega=\frac{\sin^2\alpha\sin 2\tau}{\sigma^2}.$$

‡ The formulæ for calculating these values are given in § 17.

20. Although the relations of the amplitude and phase to the angle of incidence are determined by the above observations, further investigation is necessary to ascertain the cause of the very marked dispersion first found by Righi, and which I also confirmed during my observations *. Further, the theory just enunciated gives a simple relation between the amplitudes of the magnetic components of the light on polar and equatorial reflexion, so that it can be further verified by this means.

This research was carried out in the Physical Laboratory of the University of Leyden. I have to thank the Director, Prof. H. Kamerlingh Onnes, most heartily for the interest which he showed during its progress, and for the many acessories which were placed at my disposal.

XXXV. *On the Change in the Absorption-Spectrum of Cobalt Glass produced by Heat.* *By* Sir John Conroy, *Bt., M.A., Fellow and Bedford Lecturer of Balliol College, and Millard Lecturer of Trinity College, Oxford* †.

Sir David Brewster made some experiments on the influence of heat on the absorbing power of coloured media, and states in his 'Treatise on Optics' (edit. 1853,

* It is remarkable that the dark band in the analyser never showed the least trace of colour.

† Communicated by the Physical Society: read February 13, 1891.

p. 174) that he "was surprised to observe that it produced opposite effects upon different glasses, diminishing the absorbing power in some, and increasing it in others." He found that the transparency of a piece of purple glass was much increased on heating, whilst that of a yellowish-green glass and of a red glass was diminished; the purple glass recovered its colour on cooling, the other two did not do so completely.

Feussner (*Fortschritte der Physik*, 1867, p. 237) made some observations on the effect of heat on the absorption-spectra of substances in solution.

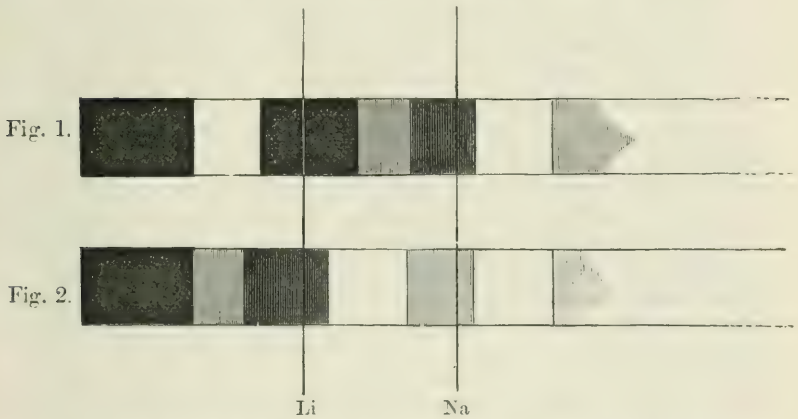
No observations on the effect of heat on the transparency of solid substances for rays of different refrangibilities except those of Sir David Brewster appear to have been published, although, of course, the change of colour which borax blow-pipe-beads containing certain metallic oxides undergo on cooling is well known. I therefore venture to communicate to the Physical Society some determinations which I have recently made on the changes produced by heat in the absorption-spectrum of cobalt glass.

The absorption-spectra of coloured glasses are not, as a rule, very characteristic, and merely show a continuous absorption extending through a considerable portion of the spectrum. Cobalt glass, however, as is well-known, has a characteristic absorption-spectrum consisting of three dark bands, in the red, yellow, and green, with a considerable amount of absorption between the first two; so that with a rather deeply coloured glass the transmitted light consists merely of the extreme red, some yellowish-green, and the blue and violet rays.

A small piece of this glass was heated by means of a medium-sized Bunsen (15 millim. tube), the glass being supported on, and nearly surrounded by, combustion-furnace tiles. It was found that in this way the glass could be heated till the edges began to soften and were visibly red, without much risk of its cracking either whilst being heated or during its subsequent cooling. An ordinary gas-jet was used as the source of light, and the light transmitted by the glass examined with a spectroscope; a small direct-vision one being used, as it was found that the changes in the spectrum were less distinctly seen with a spectroscope of greater dispersive power.

The absorption-spectrum of the cold glass is represented in fig. 1, which is drawn to an arbitrary scale, and not to one of wave-lengths. On gradually heating the glass, the absorption between the two first dark bands, those in the red and yellow,

diminishes. The band in the red moves towards the least refrangible end of the spectrum, whilst those in the yellow and green retain their position, but become less distinct. Fig. 2 represents the spectrum of the hot glass.



As the glass is heated the intensity of its colour decreases; as it cools it recovers its original colour, and the absorption-spectrum changes back into that represented by fig. 1.

The position of the bands was measured, and the table gives the results, reduced to a scale of wave-lengths.

	Cold Glass.	Hot Glass.	Dr. Russell's Values.
Band I.	700	712	665
	636	655	632
Band II.	608	608	605
	580	583	588
Band III.	565	558	555
	indistinct	indistinct	

Dr. W. J. Russell, in a paper on the "Absorption Spectra of Cobalt Salts" (Proc. Roy. Soc. xxxii. p. 258) gives a map of the spectrum of cobalt glass drawn to a scale of wave-lengths. The position of the bands, as shown in Dr. Russell's map, is given in the third column of the above table.

The agreement between the values obtained with the cobalt glass when cold and those from Dr. Russell's map, except for the least refrangible edge of the first band, are as close as, perhaps, could well be expected, considering the small dispersion of the spectroscope used for the measurements, and the difficulty of determining the exact position of an absorption band. There is considerable difference with regard to the position of the least refrangible edge of band 1; that

the position assigned to it for the particular sample of glass used in these experiments is, at least, approximately correct, is shown by the fact that the red lithium line of wave-length 670 lies within the band, both when the glass is cold and when it is hot.

These observations and those of Feussner show that the absorption-spectra of some substances vary with the temperature, as indeed might have been anticipated from the behaviour of the blowpipe-beads already referred to. In the case of solutions this may be due to the formation of different hydrates, or to the partial dissociation of the substances; but in the case of a solid substance, like cobalt glass, an actual change in the chemical constitution of the glass at a temperature considerably below its fusing-point does not seem very probable, although the well-known effects to light in causing glass which has been decolorized with manganese dioxide to become purple seems to show that such a change is not impossible.

XXXVI. *On Allotropic Silver.* *By* M. Carey Lea*.

Part II.—*Relations of Allotropic Silver with Silver as it exists in Silver Compounds.*

THE first part of this paper was devoted to the examination of one of the well-marked forms of allotropic silver—the gold-coloured. The blue form in its soluble and insoluble varieties will be more particularly described in a future paper. The subject at present to be considered is the relation existing between the allotropic forms of silver taken generally and silver as it exists in its compounds and more especially in the silver haloids.

It is a well established law that when a substance is capable of existing in two forms, of which one is a polymer of the other, the polymeric form possesses greater density and less chemical activity. Combination is usually accompanied with loss of activity, and the polymerization of a body consists in its combination with itself. When a substance is capable of existing in two allotropic forms and of being converted from the one to the other by pressure, the body resulting from pressure is always the more dense of the two and is a polymer of the first†. In the case of allotropic silver these laws appear to

* From an advance proof communicated by the Author.

† See examination by Spring of the effect of pressure, *Ber. D. Ch. Ges.* xvi. p. 1002, 1003.

be verified. I have shown elsewhere that gold-coloured silver has a specific gravity of 8·5, whilst that of normal silver is 10·5 to 10·6. The greater chemical activity of the gold-coloured form is demonstrated by its greater affinity for oxygen, sulphur, and the halogens. Also it is conspicuous by the remarkable facility with which it passes from the one state to the other. Spring, in the examinations above referred to, used pressures of many thousands of atmospheres. Allotropic silver is changed readily to normal by the mere pressure of the finger or by a temperature of 100° C.

One form of allotropic silver has the property of solubility in water. The solution of a solid in a liquid is often accompanied by change to a more simple molecular structure. Hitherto the only solvent known for a metal has been another metal, and the behaviour of metals when so dissolved has been the subject of late years of very interesting examinations by several chemists. Ramsay* examined the lowering of the vapour-pressure of mercury by other metals dissolved in it. Heycock and Neville examined the fall in the freezing-point of metals, more especially of tin, caused by the solution in it of other metals†. Both of these investigations led directly to the conclusion that in the case of a dilute solution of one metal in another, the dissolved metal existed in the atomic form. (In each case a few metals gave exceptional results, but silver was not amongst these.) Tammann's investigations on the alloys of mercury led to precisely similar general deductions. Great weight attaches to conclusions supported in these several ways.

The fact that a metal in dissolving in another metal appears to assume the atomic form affords no positive proof that it does the same in dissolving in water. In fact the solution of a metal in water is something so new that we have little ground for argument by comparison. So far, however, as the above mentioned analogy may be considered to go, it rather tends to the view that the solubility of silver may be due to its having assumed a very simple and perhaps an atomic form. It may be said therefore that all considerations tend to show that the allotropic forms of silver taken as a whole have a more simple molecular nature than what I have described as the intermediate form, and that this again is more simply constituted than ordinary silver.

In the present case we have to consider three distinct forms, (1) allotropic, (2) intermediate, (3) ordinary silver. We notice that (1) can with the utmost facility and in several ways be

* Roy. Soc. Trans. 1889, p. 521; also Wiedemann, *Referate*, 1889, p. 993.
† Journ. Chem. Soc. 1890, p. 376; 'Nature,' Jan. 1891, p. 262.

converted into (2) and (3) and that (2) can always be converted into (3), but that *these transformations can by no possibility be reversed*. To convert ordinary silver into allotropic we must as a first step dissolve it in an acid: that is, *convert it from a polymerized to an atomic form*, and only from this atomic form can allotropic silver be obtained.

Bearing this capital fact in mind and considering the respective properties exhibited by the three forms of silver, it may be allowable to adopt as a working hypothesis the view that they may represent the three possible molecular forms of silver, viz. *atomic, molecular, and polymerized*.

As silver in its compounds and in its saline solutions exists in the atomic form, it is easily conceivable that when it separates from such solutions by reduction, the atoms may or may not unite to molecules. Usually elementary atoms do so unite, but the phenomena of nascent action indicate that this union does not take place at the instant of separation, and it is at least conceivable that under particular circumstances this union may be prevented. In some cases no such union takes place. At least four metals exist in the form of vapour in the atomic state. Whether this state continues after condensation we do not know, but there is no impossibility but what such may be the case. Similarly allotropic silver may represent an atomic form: if this were so, it should exhibit more active affinities for oxygen and the halogens than the ordinary form. Also it should readily pass into the ordinary form. And these properties are undoubtedly exhibited by allotropic silver.

There is no branch of chemical statics in which our knowledge is so defective as it is in relation to the molecular constitution of solids and more especially of the metals. All that can be said is that in metals, as we ordinarily know them, this constitution is probably very complex, the molecules containing many atoms. When substances assume a variety of forms differing from each so much as do the forms of silver, we must either adopt a theory of the character now suggested or else we must suppose that the different forms are differently polymerized. To decide which is most probable of these two views, it is best to examine as to whether an analogy can be traced between these allotropic forms of silver and silver where it is known to exist in an atomic form, namely, in the compounds. For this comparison the silver haloids (and chiefly silver chloride) will be taken.

Action of Forms of Energy on Silver Haloids. Parallelism with Allotropic Silver.

It is a familiar fact that certain forms of energy, light especially, affect the silver haloids. In view of what has been already said as to the action of all forms of energy on allotropic silver, it seemed desirable to make a general examination as to their action on the silver haloids and thus to determine how far a parallelism could be traced.

It is to be observed that the action of different forms of energy on the silver haloids is apt to be partial: the influence seems to be antagonized by opposing and almost equally matched forces. Thus in the case of light, its tendency to condense the atoms of silver to molecules is largely counteracted by the strong affinity of chlorine for *atomic* silver. The action of high-tension electricity, as will presently be seen, is similar to that of light in that it produces a visible effect. In the case of heat and of contact action on these silver haloids, it will be shown that there is at first a mere indication of effect, invisible to the eye, but readily brought out by the action of a reducing agent, as described below. The action of each form of energy seems to be almost counteracted by opposing affinities. But in every case action does take place and *always in a direction corresponding to the action of that form of energy upon allotropic silver.*

High-tension electricity, it is well known, impresses sensitive films of silver haloids, which on development exhibit remarkable ramifications. When electric sparks are passed through paper on which a coating of silver chloride has been made, the point of passage of each spark is marked by a minute circle of violet colour indicating a visible change, probably to a subchloride.

Mechanical force.—More than twenty years ago I noticed that by a slight pressure, an invisible effect, capable of development, could be impressed on silver iodide. Lines drawn with a glass rod or any other hard, neutral substance were reproduced. An embossed card pressed gently on the film, gave an image of all its details on development. These experiments were extensively repeated by others with concordant results.

I have recently repeated them with silver bromide with similar effect.

Heat.—To determine the effect of heat on silver bromide, pieces of bromide paper were placed in a desiccator (of course using inactive light) and heated to the extent indicated. For each piece so heated, a corresponding piece cut from beside

it in the same sheet was preserved, and these two pieces, that heated (after complete cooling) and that not heated, were placed side by side in an oxalate developer. Comparison between these developments indicated the effect of the heat. The following results were obtained :—

A piece kept for 3 minutes at 145° C. was strongly affected and blackened quickly in the developer, the companion piece remaining white.

A piece kept for 15 minutes at a temperature commencing at 131° C. and ending at 136° was still more thoroughly affected than the foregoing, the longer exposure more than making up for the lower temperature. Companion piece remained white.

A piece kept for 8 minutes at a temperature 107° to 108° was distinctly but not strongly affected. Companion piece as before.

A piece kept for 17 minutes at a temperature of 100° to 102° was almost unaffected. A long and careful development brought out a faint difference between the piece so heated and its companion piece.

It was found that to obtain accuracy in determinations such as these, the paper must rest on a glass, and not a metal, shelf in the desiccator, as the metal shelf is always hotter than the air by which the thermometer is affected. In using a metal shelf, if the paper curled by reason of the heat, the part that rested on the shelf developed darker than that which was simply acted on by the air. By substituting a glass shelf this difference of effect disappeared.

The result of the foregoing and other experiments was that the effect of heat on AgBr commences at about 100° C., that up to 108° it is still slight and acts slowly, but that at 120° to 126° a strong action commences, which further increases as the temperature is raised. The analogy with allotropic silver is well marked.

It may at first seem strange that a temperature of 100° C. should produce a permanent change in a substance which will bear a high heat without decomposition, but the explanation lies in the presence of water in the former case. When silver bromide is formed in paper and dried in the air, it still retains moisture. Even at 100° C. this moisture is not driven off. A silver haloid requires to be heated to a temperature between 130° and 140° for several hours before it ceases to lose weight. Therefore in all the foregoing cases moisture must have been present.

It remains to be shown that by a sufficiently long exposure to a moderate heat in the presence of moisture, a visible decomposition results.

For this purpose silver chloride was precipitated with an excess of hydrochloric acid, after thorough washing was placed in a glass tube of about a centimetre in internal diameter and half a metre long, and was sealed up with a blast lamp. During all these operations the chloride was thoroughly protected from light. Five of six centimetres cube of pure water was first added to the chloride. It was intended to exclude completely or almost completely the effect of pressure and to act on the chloride as far as possible by heat only, and for this reason a longer tube was used and one end only was immersed in the chloride-of-calcium bath, the other end remained cold throughout the operation.

The silver chloride formed itself into a compact plug and was forced by the steam which generated below it up to the middle of the tube. This effect, though not intended, answered very well, as the chloride was kept constantly under the influence of steam at about 100°. It soon began to darken and at the end of three or four hours all the lower part was violet-brown, the upper part grey, the change taking place entirely through the mass. Some thin smears of silver chloride on the lower inside part of the tube were completely blackened.

On opening the tube next day there was no escape of gas. The water sealed up with the silver chloride had acquired a faint but distinct alkaline reaction, showing that enough alkali had been dissolved from the glass to overcome any acidity arising from decomposition of the chloride. The water contained traces of alkaline chloride.

A similar examination was made with silver bromide precipitated with excess of hydrobromic acid and thoroughly washed with distilled water. The action of diffuse light on silver bromide is very different from that on silver chloride. A portion of that prepared as above mentioned changed in diffuse light very quickly from yellow to greenish yellow, but after that first change the alteration was extremely slow and in an hour had only reached to a dirty greenish grey. The action of direct sunlight was quite different: fifteen minutes' exposure changed the greenish grey to dark chocolate-brown.

In the tube the silver bromide did not form a plug like the chloride, but separated into balls which remained in the bottom of the tube. By keeping the chloride-of-calcium bath considerably above 100° C., the water in the tube was kept actively boiling: it condensed in the upper part of the tube and returned. Six hours of this treatment only brought the bromide to the same greenish colour which it would have acquired by a few minutes' exposure to diffuse light.

The conclusion to be drawn as respects both the silver haloids is that they undergo actual decomposition by the action of moist heat, but that this effect is much more marked in the case of chloride than that of bromide *.

Chemical action.—Dilute sulphuric acid quickly changes allotropic silver to normal, and therefore if the parallelism which I have indicated really exists, marks made on bromide paper with dilute sulphuric acid should be capable of development.

The experiment was made by drawing characters on silver bromide with a glass rod dipped into sulphuric acid diluted with twice its bulk of water. After allowing the acid to remain in contact for two or three minutes, the paper was immersed in running water and was washed for an hour or two.

On applying the oxalate developer nothing appeared. Feeling confident that some effect must be produced, the experiment was repeated several times and the results were closely examined. On one specimen it was found that the characters had appeared, but reversed—that is, lighter than the ground, which had darkened by the development being pushed. This at once gave a clue: it showed that traces of the acid adhered too strongly to be removed by washing, and by locally checking the development interfered with the reaction. Accordingly, next time, after a very short washing, the paper was immersed in water to which a trace of ammonia had been added, and after ten or fifteen minutes' action the ammonia was thoroughly washed out. The result was striking: as soon as the developer was applied, the characters which had been traced with acid came out strongly as brown marks on a white surface.

Cold sulphuric acid, even undiluted, is generally held to have no action on silver haloids, but it is well-known that the hot strong acid decomposes them. The foregoing experiments leave no doubt that the cold dilute acid produces an initial effect invisible to the eye but revealed by greater tendency to give way under the action of a reducing agent. This action of the acid comes therefore exactly into line with that of light and heat. In all three cases an effect is produced inappreciable until a reducing agent is applied. But in all three cases the agent which produced this invisible effect is capable, by

* Light and heat act differently on silver chloride. Heat cannot decompose it in the absence of moisture, but light can. This was proved by an investigation made by the writer in 1880, in which it was shown that fused silver chloride poured into petroleum and exposed after cooling to the sun's rays was instantly blackened.

continued action under favourable conditions, of bringing about a visible change without the aid of a reducing agent.

Light.—The silver haloids in their sensitiveness to light show an important relationship to that of allotropic silver. When, for example, silver chloride precipitated with an excess of hydrochloric acid is exposed to light, the darkened product contains apparently no metallic silver* (it is probable that the trace of silver given up to nitric acid may arise from the decomposition of a very small quantity of subchloride). However this may be, the subchloride, and not metallic silver, is the essential product.

This has always seemed a very enigmatical result. Two combinations of silver and chlorine exist—the one very stable, capable of fusion without decomposition; the other so unstable that it can hardly exist isolated, and yet the stable compound is rapidly broken up by light, even by a weak diffuse light, whilst the unstable compound resists many days' exposure to the strongest sunlight.

In examining the action of light upon allotropic silver (see Part I.), an equally remarkable effect was described. Although all the other forms of energy applied readily and quickly convert allotropic to ordinary silver, light (at ordinary temperatures) fails to effect this change even by exposures lasting for several months. If we conceive that the atomic form of silver which exists in AgCl corresponds to the allotropic form, and that the more condensed form of subchloride corresponds to the "intermediate form," we shall obtain a reasonable explanation of the action of light.

The inability of light to carry the change which it produces in allotropic silver beyond the "intermediate form" exactly corresponds to its inability to carry the decomposition of silver chloride further than to subchloride or rather to photochloride. (It is understood that the silver chloride here spoken of is that which is formed by precipitation with excess of hydrochloric acid.) This explanation appears to remove a real difficulty, and at the same time establishes a perfect parallelism between that action and the action of light on allotropic silver.

Although the foregoing study of the silver haloids was made for the purpose of fixing the relations which exist between them and allotropic silver, the results nevertheless have

* In some (unpublished) experiments made some years ago to test this point, I found that silver chloride exposed for several days to strong sunlight under water, with frequent stirring up, and subsequent washing, yielded only a trace of silver to strong cold nitric acid after a contact of an hour.

much interest in relation to the haloids themselves and place their nature in a somewhat new light. For it is shown that these haloids, though substances in some respects of very great stability, have their equilibrium so balanced as to respond to the slightest influence, not merely of light, but of any form of energy, not receiving a momentary but a permanent impression which, though so slight as to be invisible, still greatly increases the tendency of the molecule to fall to pieces under the action of a reducing agent. Further, four of these forms of energy, light, heat, electricity, and chemical action, when more strongly applied, totally disrupt the molecule. One form of energy, mechanical force, though capable of producing the invisible effect, makes an apparent exception in respect of this ability to disrupt. This matter is now under examination, and it will probably be shown hereafter that the analogies are complete and without exception.

The same completeness holds with regard to the analogies which form a principal subject of this paper, namely, those existing between allotropic silver and the metal as it exists in the salts of silver. No other salts but those of silver show this wonderfully balanced equilibrium, sensitive to all forms of energy. But allotropic silver also shows an almost exactly similar capacity to respond to the influence of energy in all its manfestations by undergoing changes of a like character.

The inferences to be drawn from the foregoing seem to be as follows. That silver may exist in three forms: 1st. Allotropic silver which is protean in its nature; may be soluble or insoluble in water, may be yellow, red, blue, or green, or may have almost any colour, but in all its insoluble varieties always exhibits plasticity, that is, if brushed in a pasty state upon a smooth surface its particles dry in optical contact and with brilliant metallic lustre. It is chemically active. 2nd. The intermediate form, which may be yellow or green, always shows metallic lustre, but is never plastic and is almost as indifferent chemically as white silver. 3rd. Ordinary silver.... Further, that allotropic silver can always be converted, either into the intermediate form, or directly into ordinary silver; that the intermediate form can always be converted into ordinary silver, but that these processes can never be reversed, so that to pass from ordinary silver to allotropic it must first be rendered atomic by combination, and then be brought back to the metallic form under conditions which check the atoms in uniting. That allotropic silver is affected by all forms of energy, and that this effect is always in one direction, namely,

towards condensation. That the silver haloids are similarly affected by the same agencies. That a remarkable parallelism is noticeable between the two actions, especially if we take into account that in the haloids the influence of energy is to some extent restrained by the strong affinity which the halogens show for atomic silver. There is therefore reasonable ground to suppose that in the silver haloids silver may exist in the allotropic form.

Philadelphia, February 1891.

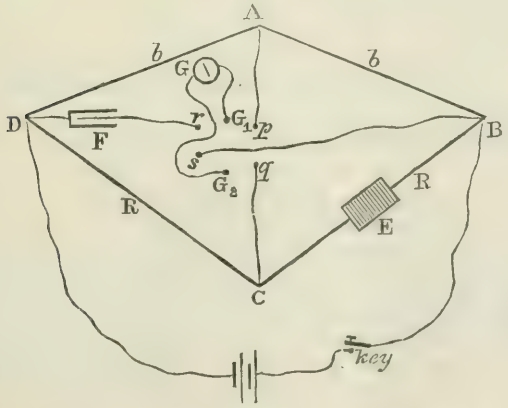
PM 31 (1891)

XXXVII. *On Coefficients of Induction.* *By* A. Anderson, *M.A., Professor of Natural Philosophy in Queen's College, Galway.**

1. THE following method of measuring the coefficient of self-induction of a coil is somewhat similar to that of Maxwell ('Electricity and Magnetism,' vol. ii. art. 778), inasmuch as a condenser is employed. But it is not a null method; and, although not absolutely necessary for rough determinations, it is desirable to use a ballistic galvanometer on account of the ease with which the throws of the needle can be observed, and because less adjustments and observations have to be made.

In fig. 1, E is the coil whose inductance is to be found.

Fig. 1.



One pole of the condenser F is joined to D, and the other to a mercury-cup r. G_1 and G_2 are mercury-cups forming the

* Communicated by the Author.

terminals of the galvanometer, and p, q, and s are mercury-cups connected respectively with A, C, and B. A rocking-key can simultaneously connect G_1 with p and G_2 with q, or G_1 with r and G_2 with s, the galvanometer being in the former case in the branch AC and in the latter in BD, in series with the condenser. The branches AB AD are equal inductionless resistances, and DC, which is also inductionless, is adjusted till as perfect a balance as possible is obtained. When the battery-circuit is made or broken, the galvanometer being in the branch AC, there is a throw of the needle due to the passage through this branch of a quantity of electricity equal to $L\left(\frac{dc}{dx}\right)_{x=0}$, where L denotes the coefficient of self-induction of E, and c the current in the galvanometer, when an additional resistance x is put in the branch BC. The current c is equal to $Eb\Delta x/\Delta$, E being the E.M.F. of the battery, and Δ the determinant

$$\begin{vmatrix} a+2R+x, & -R-x, & -R \\ -R-x, & b+G+R+x, & -G \\ -R, & -G, & b+G+R \end{vmatrix}$$

in which a is the resistance of the battery, R of the coil, and G of the galvanometer. Since

$$\left(\frac{dc}{dx}\right)_{x=0} = \left(\frac{Eb}{\Delta}\right)_{x=0},$$

we easily find

$$\left(\frac{dc}{dx}\right)_{x=0} = \frac{Eb}{(b+2G+R)[a(b+R)+2bR]},$$

and therefore the quantity of electricity is

$$\frac{LEb}{(b+2G+R)[a(b+R)+2bR]}.$$

If, by means of the rocking-key, the galvanometer be put in BD, and the battery-circuit made or broken as before, a quantity of electricity will pass through the galvanometer equal to $K(V_1-V_2)$, where K is the capacity of the condenser and V_1-V_2 the final difference of potential between the points B and D. If the capacity K be adjusted till the throw of the needle is the same as before, we have

$$L=K\frac{V_1-V_2}{Eb}(b+2G+R)[a(b+R)+2bR].$$

which reduces to

$$L = 2KR(b + 2G + R),$$

since

$$(V_1 - V_2)\left(a + \frac{2bR}{b+R}\right) = \frac{2bR}{b+R}E.$$

It may not be possible, with given values of b, R, and G, and a given condenser, to make the throws the same. R may, however, be increased or diminished by the introduction of an inductionless resistance in series or in parallel with it, and the same is true for b and G. A slight change in the formula will then be necessary. If, in this way, we find two nearly equal values of K for one of which the throw of the needle is greater and for the other less than that of the former throw, the correct value of K may be found by proportional parts. But a much better method is to use a ballistic galvanometer, in which case no adjustment of resistances beyond that of getting a perfect balance is required. The two angles of throw α and α' are simply observed, and the coefficient of self-induction is given by the formula

$$L = 2KR(b + 2G + R) \sin\frac{\alpha}{2} \sin\frac{\alpha'}{2}.$$

The following determination of the self-induction of a coil may be given as an example. The coil was a circular coil of mean radius 20·9 centim. wound in a rectangular groove of breadth 1·894 centim. and depth 1·116 centim., and having 278 turns. The galvanometer was an ordinary reflecting galvanometer with a resistance of 164·8 ohms, the controlling magnet being placed so as to make the sensibility as great, and the time of swing as long, as possible. An inductionless resistance of 100 ohms was put in series with the coil, and the resistances of the branches AB and AD were each 10 ohms. A balance was roughly obtained by making the branch CD 150 ohms, and, in the absence of better means, an almost perfect balance by adding to CD a wire whose resistance was subsequently found to be ·51 ohm. The resistance of the branch CD or CB was therefore 150·51 ohms. The following numbers are the means of several readings which agreed very well together :—

Kick of needle due to self-induction of coil	= 43·208 scale-divisions.
Kick due to charge or discharge of condenser, capacity ·5 microfarad . . .	= 46·125 ,, ,,
Kick for capacity of ·45 microfarad	= 41·875 ,, ,,

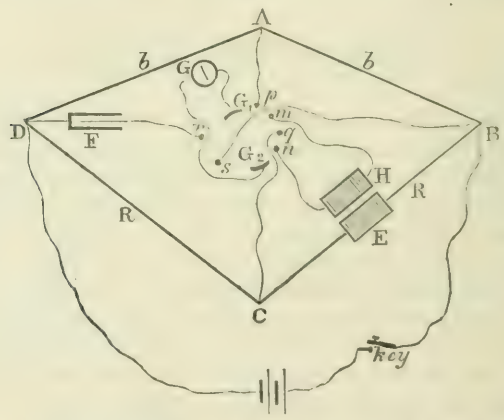
The capacity which would give a kick of 43·208 is found from these numbers to be ·4657 microfarad. The coefficient of self-induction, when reduced to absolute measure, is therefore

$$10^3 \times \cdot 9314 \times 150\cdot 51 \times 489\cdot 7 = \cdot 06865 \times 10^9,$$

or, in practical measure, ·06865 henry.

2. The method can easily be adapted to determine the coefficient of mutual induction of the coil E and another coil H, a slightly more complicated key being used. There are two additional mercury-cups m, n (fig. 2) which are the

Fig. 2.



terminals of the coil H, and the cups G_1 G_2, the galvanometer terminals, are lengthened into equal portions of a circular groove, so that the rocker, when turned round as far as possible to the left, will connect G_1 with p and G_2 with q; and, when turned to the right, G_1 with m and G_2 with n. In its middle position it can connect G_1 with r and G_2 with s. With such a key, a ballistic galvanometer of known resistance, and a condenser, we can without difficulty determine both the coefficient of self-induction of E, and the coefficient of mutual induction of E and H. Let the rocker

be placed so as to bring the coil H into circuit with the galvanometer. When the battery-circuit is completed or broken, after a balance has been obtained as before, the quantity of electricity which flows through the galvanometer is

$$M(V_1-V_2)/2R(r+G),$$

r being the resistance of the coil H, which must be previously determined, and M the coefficient of mutual induction. If α'' denote the angle of throw in this case, α, α', and K signifying the same as before, and the latter not being altered, we have

$$M=2KR(r+G)\sin\frac{\alpha''}{2}/\sin\frac{\alpha'}{2},$$

and

$$M/L=(r+G)\sin\frac{\alpha''}{2}/(b+2G+R)\sin\frac{a}{2}.$$

Of course we may, in this case also, employ an ordinary high-resistance galvanometer, but with somewhat more trouble and perhaps less accuracy.

In the following determination of a coefficient of mutual induction, although the galvanometer used was not ballistic, the throws of the needle are assumed to be, although they are not, proportional to the quantities of electricity passing through the galvanometer-coils. The resistance of the coil E was 1·003 ohm, that of H 157·7 ohms, and that of the galvanometer 164·8 ohms. The throws a'' and a' were respectively 72 and 5 scale-divisions, and K, the capacity of the condenser, was 1 microfarad.

Hence

$$M=10^3\times 2\cdot006\times 332\cdot5\times 14\cdot4 \text{ centim.}$$
$$=9315864 \text{ centim.}$$
$$=\cdot0093 \text{ henry.}$$

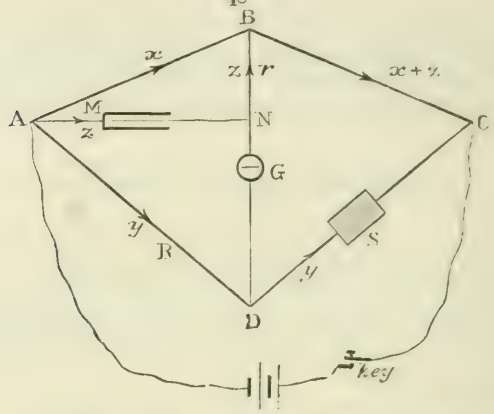
3. *Null Method of measuring the Coefficient of Self-induction of a Coil.*

In the method given in Maxwell (art. 778, vol. ii.) the current through the galvanometer at any moment is zero, but the double adjustment which is necessary is inconvenient. Two methods are given by Mr. Rimington in the 'Philosophical Magazine' for July 1887; but this condition is not fulfilled, and Mr. Rimington shows this for one of his methods. Prof. Niven's methods, given in the 'Philosophical Magazine' for September 1887, do not differ greatly from those given by Mr. Rimington.

The following method, which is but a slight modification of Maxwell's, does away with much of its impracticability.

In Maxwell's method the armatures of the condenser are connected to A and B (fig. 3), and S is the coil whose coefficient of self-induction is to be found. The only difference in

Fig. 3.



the method now given is that an adjustable resistance r is placed between B and N. Suppose a balance has been obtained so that no permanent current flows through the galvanometer. This balance will not be disturbed by changing r. Let x be the whole quantity of electricity which has passed through AB at the time t, z the whole quantity which has passed through AM, and y that through AD. Then, if K be the capacity of the condenser, and if we suppose the potential of N to be always equal to that of D, we have

$$P\frac{dx}{dt} = \frac{z}{K} + r\frac{dz}{dt},$$

$$\frac{z}{K} = R\frac{dy}{dt},$$

$$r\frac{dz}{dt} + Q\left(\frac{dx}{dt} + \frac{dz}{dt}\right) = S\frac{dy}{dt} + L\frac{d^2y}{dt^2},$$

and, therefore,

$$(r+Q)\frac{dz}{dt} + \frac{Q}{P}\left(\frac{z}{K} + r\frac{dz}{dt}\right) = \frac{S}{RK}\frac{z}{} + \frac{L}{RK}\frac{dz}{dt}.$$

Hence we have the conditions

$$QR = PS,$$

and

$$r + Q + \frac{Qr}{P} = \frac{L}{RK}.$$

The first is the condition for no permanent current; and the second, which is the condition for no instantaneous current, gives the formula

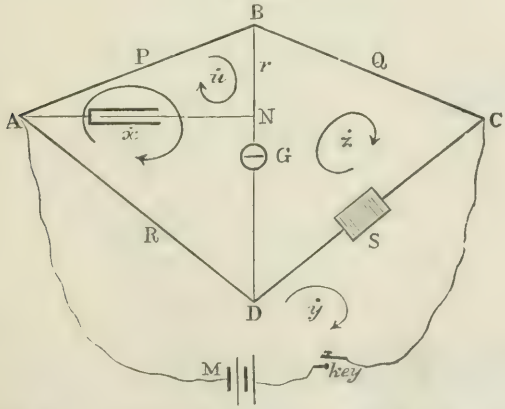
$$L = K\{r(R+S)+RQ\}.$$

If we make $r=0$, we get Maxwell's formula. The practical method immediately suggested by the above expression for L is to obtain a permanent balance in the ordinary way, and then to adjust r and, if possible, K till there is no motion of the galvanometer-needle. Or if, as in Maxwell's method, values of P, Q, R have been obtained, so that there is only a small throw of the needle when the battery-circuit is made or broken, the final adjustment may be quickly and accurately made by introducing an adjustable resistance r, and in doing this a telephone may be employed instead of the galvanometer. It is clear that, if we do this, R and Q must be such that $KRQ<L$.

However, we may make the rough adjustment, having first placed a small resistance between N and B, and subsequently adjust this till there is no kick of the galvanometer-needle or no sound in the telephone.

In order to find the relative values of the various resistances which will make the sensitiveness of the final adjustment greatest, we will calculate the quantity of electricity q which passes through the galvanometer on making or breaking the battery-circuit after the adjustment for no permanent current has been made.

Fig. 4.



Consider the system of conductors in fig. 4 as made up of the circuits DAB, DBC, MADC, and the condenser-circuit

NAB, and let the currents round these circuits be denoted respectively by $\dot{x}$, $\dot{z}$, $\dot{y}$, and $\dot{u}$. Then, if B be the resistance of the battery, G of the galvanometer, L the coefficient of self-induction of the coil in the branch DC, λ that of the galvanometer-coil, K the capacity of the condenser and u its charge, we have, employing the same notation as that used in Prof. Niven's paper

$$T=\tfrac{1}{2}L(\dot{y}-\dot{z})^2+\tfrac{1}{2}\lambda(\dot{x}-\dot{z})^2,$$

$$F=\tfrac{1}{2}\{P(\dot{x}+\dot{u})^2+r(\dot{x}+\dot{u}-\dot{z})^2+Q\dot{z}^2+R(\dot{y}-\dot{z})^2 + G(\dot{x}-\dot{z})^2+S(\dot{y}-\dot{z})^2+B\dot{y}^2\},$$

$$H=u^2/2K.$$

Hence, if x, y, z denote the total transient flow round the respective circuits during the time of setting up or destroying the permanent state at make or break of the battery-circuit, and $\dot{x}_0$, $\dot{y}_0$, $\dot{z}_0$ the steady values of the currents, we easily find:—

$$(R+S+B)y-Rx-Sz=-L(\dot{y}_0-\dot{z}_0)-\lambda(\dot{x}_0-\dot{z}_0);$$

$$(r+G)x+Sy-(r+Q+G+S)z=-L(\dot{y}_0-\dot{z}_0)-\lambda(\dot{x}_0-\dot{z}_0)-KrP\dot{x}_0;$$

$$(P+r+R+G)x-Ry-(r+G)z=-KP(P+r)\dot{x}_0.$$

Writing for $\dot{x}_0$, β, for $\dot{y}_0-\dot{z}_0$, α, and for $x-z$, q, and observing that $\dot{x}_0=\dot{z}_0$ and that $PS=QR$, we find without difficulty

$$q=\frac{K\beta P\{PQ+r(P+Q\}\quad PL\alpha}{P(Q+S)+(P+Q)(r+G)}.$$

Thus, when $q=0$,

$$L=\frac{\beta}{\alpha}K(PQ+r(P+Q)),$$

$$=\frac{R}{P}K(PQ+r(P+Q)),$$

$$=K(RQ+r(R+S)),$$

which is the same equation as before.

To estimate the sensitiveness of the final adjustment, we will calculate the ratio of the small change produced in q to the small change made in r when $q=0$.

Differentiating the above expression for q, and making $q=0$, we have

$$\left(\frac{dq}{dr}\right)_{q=0} = \frac{K\beta P(P+Q)}{P(Q+S)+(P+Q)(r+G)}.$$

If we substitute for β its value in terms of E, the electromotive force of the battery and the resistances, we find

$$\left(\frac{dq}{dr}\right)_{q=0} = \frac{EK}{\left[1+B\left(\frac{1}{P+Q}+\frac{1}{S+R}\right)\right]\left[Q+S+\left(1+\frac{Q}{P}\right)(r+G)\right]}.$$

It seems therefore advantageous to make R and P both large, and Q and r both small. Hence the very easy practical method suggested by the formula might not be so sensitive as to obtain first an approximate adjustment, and then to make the final adjustment by varying r.

The following example of the measurement of the coefficient of self-induction of a coil by this method may be given. The resistance Q being 10 ohms, and P 100 ohms, there was a permanent balance when R was made 1577 ohms, so that S, the resistance of the coil, was 157·7 ohms. A condenser of 1 microfarad capacity was then placed between A and N and the resistance r adjusted till there was no kick of the galvanometer-needle. This value of r was found to be 59 ohms, though the sensitiveness was, doubtless, not as great as might have been obtained. Substituting these values, we have

$$L=10^3\times(15770+59\times1734{\cdot}7) \text{ centim.}$$
$$=\cdot118 \text{ henry.}$$

The same method was also employed to find the coefficient of self-induction of the coil described in (1) of resistance 59·51 ohms. P was made 1000 and Q 10 ohms: and when R was 5051 an almost perfect balance was obtained. Both a telephone and a galvanometer were used in the final adjustment of r, and the value thus found was 3·65 ohms. The coefficient of self-induction is, therefore,

$$10^3\times(50510+3{\cdot}65\times5101{\cdot}51) \text{ centim.}$$
$$=\cdot0691 \text{ henry,}$$

which does not differ greatly from the previous result.

XXXVIII. *On the Application of Interference-Methods to Spectroscopic Measurements.*—I. *By* ALBERT A. MICHELSON *.

[Plate VII.]

IN a paper on "Measurement by Light-Waves" † it was shown that by substituting a refractometer for a microscope or telescope or spectroscope, the accuracy of measurement may be increased to a remarkable degree, but at the cost of resolution and definition. When the object viewed is smaller than the limit of resolution, however, then, even in the ordinary sense, these instruments possess scarcely any advantage; but if by "defining-power" is meant not the actual resemblance of the image to the object, but the accuracy with which the form or the distribution of light may be inferred, then the refractometer has remarkable advantages in both defining-power and accuracy.

This has been pointed out in the preceding paper (*suprà*, p. 256) in the case of telescopic observations. It was shown that by a proper interpretation of the "visibility-curve" the form and the distribution of light might be correctly inferred, even when the object is beyond the resolving-power of the telescope.

In the present paper it is proposed to show that the same principle holds in spectroscopic observations, and even with greater force.

In fact, a spectral line might be viewed by a telescope converted into a refractometer, and the "line" could be studied in precisely the same way as a nebulous star. Such a method, however, would multiply the necessary imperfections of lenses and prisms or gratings.

Fortunately both spectroscope and telescope may be dispensed with, by substituting the refractometer in any form which allows a considerable and steady alteration in the difference in path between the two interfering streams of light from any approximately homogeneous source.

One of the first applications of this method ‡ showed that the red hydrogen-line is a very close double; and the same is also true for the green thallium-line. Another instance of the class of problems which the method may help to solve is the effect of the velocity of the vibrating molecule in the line of sight in broadening the spectral lines.

* Communicated by the Author.

† American Journal of Science, vol. xxxix., Feb. 1890.

‡ Phil. Mag. Dec. 1887.

This question has been discussed by Ebert*, who concludes that the width of the spectral lines due to this cause is not consistent with the results obtained by interference.

Lord Rayleigh† has shown that this conclusion does not hold; and that the apparent inconsistency is, at least in part, due to the arbitrary assumption of a concentration of light at the edges of the line. Proceeding to investigate the case of uniform distribution, he arrives at the result that for this case the visibility-curve is periodic.

It will appear later that this is the fact in most, if not all, of the radiations thus far examined. This is at variance with the result obtained by Lord Rayleigh for a distribution resulting from Maxwell's law of velocities; but it is expressly stated that "the case of electric discharge may require further consideration."

The general formula for the visibility of fringes due to interference of two streams of light whose difference of path is variable, from a source which is not homogeneous, is the same as that for a source of finite area whose "parallax" is variable.

For the resulting intensity of two equal homogeneous streams of light is

$$I_1 = 4\cos^2 \pi \frac{D}{\lambda}.$$

If the light be included between wave-numbers n_1 and n_2 and the illumination from dn be $\psi(n)dn$,

$$I = \int_{n_1}^{n_2} I_1 dn = 4\int_{n_1}^{n_2} \psi(n)\cos^2 \pi D n \, dn.$$

If for n we substitute $\bar{n} + x$, in which $\bar{n}$ is the mean wave-number, and for $\psi(n)$ put $\phi(x)$, we have

$$I = \int_{-\frac{a}{2}}^{+\frac{a}{2}} \phi(x)\cos^2 \pi D(\bar{n} + x)dx.$$

Expanding and omitting the factor 2, putting

$$\int \phi(x)dx = P, \qquad \int \phi(x)\cos 2\pi D x \, dx = C,$$
$$2\pi D\bar{n} = \vartheta, \quad \text{and} \quad \int \phi(x)\sin 2\pi D x \, dx = S,$$

we have

$$I = P + C\cos\vartheta - S\sin\vartheta.$$

* Wied. *Ann.* vol. xxxvi. p. 466 (1889).
† Phil. Mag. April 1889.

If a be sufficiently small, the variations of C and S with ϑ may be neglected, and the maxima or minima occur when

$$\tan \vartheta = -\frac{S}{C},$$

or when

$$I = P \pm \sqrt{C^2 + S^2}.$$

Hence

$$V^2 = \frac{C^2 + S^2}{P^2}.$$

In the following discussion of some of the more interesting cases which have been solved, let Δ be the extreme difference in wave-length of the radiations in question, and let Δ_0 be the smallest difference which can be "resolved" by a grating having as many lines, N, as there are waves in the difference in path.

Then if $n = \frac{\Delta}{\Delta_0}$, we have

$$n = \frac{\lambda^2 a}{\lambda / N} = D a.$$

I. $$\phi(x) = \text{constant}.$$

This case has already been treated, and the resulting visibility-curve is

$$V = \frac{\sin \pi n}{\pi n}.$$

II. $$\phi(x) = \sqrt{r^2 - x^2}.$$

This case has also been solved; and if J_1 represent Bessel's function of order unity, the result is

$$V = \frac{J_1(\pi n)}{\pi n}.$$

III. $$\phi(x) = \cos \pi \frac{x}{a}.$$

The more general case $\cos m\pi \frac{x}{a}$ gives

$$V = \frac{\frac{\sin \frac{1}{2}(m-2n)\pi}{\frac{1}{2}(m-2n)\pi} + \frac{\sin \frac{1}{2}(m+2n)\pi}{\frac{1}{2}(m+2n)\pi}}{2 \frac{\sin \frac{1}{2} m\pi}{\frac{1}{2} m\pi}}.$$

This for $m=1$ reduces to

$$V=\frac{\cos n\pi}{1-4n^2}.$$

IV. $$\phi(x)=\cos^2 m\pi\frac{x}{a}, \quad \text{or} \quad \sin^2 m\pi\frac{x}{a}$$

$$=1\pm\cos 2m\pi\frac{x}{a}.$$

$$V=\frac{\dfrac{\sin n\pi}{n\pi}\pm\frac{1}{2}\left[\dfrac{\sin(m+n)\pi}{(m+n)\pi}+\dfrac{\sin(m-n)\pi}{(m-n)\pi}\right]}{1\pm\dfrac{\sin m\pi}{m\pi}}.$$

The following cases are of interest:—

For $m=0$ or ∞, $\quad V_0=\dfrac{\sin n\pi}{n\pi}$,

„ $m=1, 3, 5,$ &c., $\quad V=V_0\left(1\pm\dfrac{n^2}{m^2-n^2}\right)$,

„ $m=2, 4, 6,$ &c., $\quad V=V_0\left(1\mp\dfrac{n^2}{m^2-n^2}\right)$.

V. $$\phi(x)=\cos^p\pi\frac{x}{a}.$$

This case deserves special notice, as many of the others may be accurately or approximately represented by it.

In this, as in all symmetrical functions, the term S vanishes, and

$$V=\frac{\int_0^a\cos^p\pi\frac{x}{a}\cos\lambda\pi Dx\,dx}{\int_0^a\cos^p\pi\frac{x}{a}\,dx}.$$

Putting $\pi\dfrac{x}{a}=w$ and $2Da=q$, this becomes

$$V=\frac{\int_0^{\frac{\pi}{2}}\cos^p w\cos qw\,dw}{\int_0^{\frac{\pi}{2}}\cos^p w\,dw}=\frac{[\Gamma(\frac{1}{2}p+1)]^2}{\Gamma\left(\dfrac{p+q}{2}+1\right)\Gamma\left(\dfrac{p-q}{2}+1\right)}.$$

For $V=0$ we have

$$\Gamma\left(\frac{p\pm q}{2}+1\right)=\infty;$$

whence

$$\frac{p \pm q}{2} + 1 = 0,\ -1,\ -2,\ \&c.,$$

or, since $n = \frac{q}{2}$,

$$n = \frac{p}{2} + 1 + a,$$

a being any positive integer.

The visibility-curve for this case has, therefore, the remarkable property of vanishing at equal intervals, with the exception of the first, which is $\frac{p}{2}+1$ times as great.

Thus, if N_m be the number of waves in the difference in path at the mth disappearance, then

$$N_m - N_{m-1} = \frac{\Delta}{\lambda} = M\ ;$$

but

$$N_1 = \left(\frac{p}{2} + 1\right)\frac{\Delta}{\lambda}.$$

For example,

If $p=0$ (rectangle), $N_1 = M$,

$p=\frac{1}{2}$ (approx. circle), $N_1 = 1{\cdot}25\ M$,

$p=1\left(\cos \pi \frac{x}{a}\right)$, $N_1 = 1{\cdot}5\ M$,

$p=2\left(\cos^2 \pi \frac{x}{a}\right)$, $N_1 = 2{\cdot}0\ M$.

Thus the first interval determines the shape of the intensity-curve, while the succeeding ones measure the width.

VI. $$\phi(x) = e^{-p\frac{x^2}{a^2}}.$$

This is the distribution resulting from Maxwell's law; the resulting curve is

$$V = e^{-\frac{\pi^2 n^2}{p}},$$

which is not periodic. [If $x=\frac{1}{2}a$ for $y=\frac{1}{2}$, $p=4 \log 2$.]

VII. *Double Source.*

The general equation $V^2 = \frac{C^2+S^2}{P^2}$ may be put in a more useful form in the case of two distinct symmetrical sources.

Putting $(z-b)$ for $x<0$, and $z+b$ for $x>0$, $\psi_1(z)$ for $\phi_1(z-b)$, and $\psi_2(z)$ for $\phi_2(z+b)$, Z_1 for $\int \psi_1(z) \cos 2\pi Dz \,.\, dz$, and Z_2 for $\int \psi_2(z) \cos 2\pi Dz \,.\, dz$, P_1 for $\int \psi_1(z) dz$, and P_2 for $\int \psi_2(z) dz$, we have

$$V_{11}^2 = \frac{Z_1^2 + Z_2^2 + 2Z_1 Z_2 \cos 2\pi n_{11}}{(P_1 + P_2)^2}.$$

But $V_1 = \frac{Z_1}{P_1}$, and $V_2 = \frac{Z_2}{P_2}$; hence

$$V_{11}^2 = \frac{P_1^2 V_1^2 + P_2^2 V_2^2 + 2P_1 P_2 V_1 V_2 \cos \pi n_{11}}{(P_1 + P_2)^2}.$$

If n_{11} is small, that is, if the centres of the two sources are close together,

$$V_{11} = \frac{P_1 V_1 + P_2 V_2}{P_1 + P_2},$$

and if there are several sources whose centres nearly coincide,

$$V_{11} = \frac{\Sigma P_n V_n}{\Sigma P_n}.$$

If the two sources are alike, excepting a constant factor h, which may represent intensity,

$$V_{11}^2 = \frac{h^2 + h_1^2 + 2hh_1 \cos ka_2}{(h + h_1)^2} V^2.$$

Thus, if $h = h_1$,

$$V_{11}^2 = \cos^2 \pi n_{11} \,.\, V^2;$$

and, generally, if $h_1 = mh$,

$$V_{11}^2 = \frac{m^2 + 1 + 2m \cos ka}{(m+1)^2} V^2.$$

If the two sources are small when compared with their distance, $V^2 = 1$.

VIII. *Multiple Source.*

If the sources are all equal, equidistant, and symmetrical, and $n_1 = \frac{\Delta_1}{\Delta_0}$, where Δ_1 is the common interval, and $n = \frac{\Delta}{\Delta_0}$, where Δ is the extreme interval, then

$$V_m = V \frac{n_1}{n} \frac{\sin \pi n}{\sin \pi n_1}.$$

Thus if $\phi(x) = \cos^2 \pi \frac{x}{a}$,

$$V_1 = \frac{\sin \pi n_1}{\pi n_1} \cdot \frac{1}{1 - n_1^2}.$$

This gives

$$V_m = \frac{\sin \pi n}{\pi n} \cdot \frac{1}{1-n^2},$$

or

$$V_m = \frac{\sin \pi n}{\pi n} \frac{m^2}{m^2-n^2},$$

which agrees with IV.

IX. $\phi(x) = 1 + \frac{x}{e}$, $(x<0)$, $\qquad \phi(x) = 1 - \frac{x}{f}$, $(x>0)$.

Putting $2\pi D = k$, we have

$$C = \frac{1}{k^2 e}(1-\cos ke) + \frac{1}{k^2 f}(1-\cos kf),$$

$$S = \frac{1}{k^2 e}\sin ke - \frac{1}{k^2 f}\sin kf,$$

$$P = \tfrac{1}{2}(e+f).$$

If, now,

$$n_1 = r_1 n = \frac{ke}{2\pi},$$

$$n_2 = r_2 n = \frac{kf}{2\pi},$$

and

$$n = \frac{k(e+f)}{2\pi},$$

we have

$$V^2 = \frac{1 - r_2 \cos 2\pi r_1 n - r_1 \cos 2\pi r_2 n - 2 r_1 r_2 \sin^2 \pi n}{2 r_1^2 r_2^2 \pi^4 n^4}.$$

If $r = r_1 = \frac{1}{2}$,

$$V = \frac{\sin^2 \frac{\pi n}{2}}{\left(\frac{\pi n}{2}\right)^2}.$$

If $f = 0$, $e = a$, and

$$k^2 C = \frac{1}{a}(1-\cos ka),$$

$$k^2 S = \frac{1}{a}(\sin ka - ka);$$

whence

$$V^2 = \frac{1}{\pi^2 n^2}\left[1 + \frac{\sin^2 \pi n}{\pi^2 n^2} - 2\frac{\sin 2\pi n}{2\pi n}\right].$$

In the case of an unsymmetrical source, it is possible to

determine the position of the brighter portion by gradually increasing the difference in path from zero. If the fringes are thereby displaced in the positive sense from the position calculated from the mean wave-length, then the brighter edge lies toward the violet.

If the line is a double, the displacement relatively to the position calculated from the brighter source is given by the formula

$$\tan 2\pi n = \frac{\sin 2\pi \frac{N}{M}}{r + \cos 2\pi \frac{N}{M}},$$

in which n is the displacement in the fractions of a wave, N is the number of waves in the difference in path, M is the number of waves between two successive minima of distinctness, and r is the ratio of the intensities.

The cases discussed in the preceding work are illustrated by the figures in Plate VII., which give the function representing the distribution of light in a spectral line together with its corresponding visibility-curve *.

The equation for the visibility of the interference-fringes has been somewhat arbitrarily assumed to be the ratio of the sum to the difference of the intensities of the bright and dark fringes ; that is,

$$V = \frac{I_1 - I_2}{I_1 + I_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If we assume that the visibility is the greatest value of

$$\frac{-\frac{dI}{d\phi}}{\frac{1}{2}(I_1 + I_2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and also that the intensity of the fringes may be represented by

$$I = H + K \cos \phi,$$

* The value of V as deduced from the general formula is necessarily positive; so that there are no reversals of the fringes. There will be, however, a change of phase, which is given by the formula

$$\tan \vartheta = \frac{S + \frac{dC}{d\vartheta}}{C - \frac{dS}{d\vartheta}}.$$

In the case of a symmetrical function this change may be half a period; and it would not be incorrect to draw the corresponding parts of the curve below the axis.

we have in either case

$$V = \frac{K}{H}.$$

But if we define V as the maximum value of

$$\frac{-\frac{dI}{d\phi}}{I}, \quad \ldots \ldots \ldots \quad (3)$$

we have

$$V = \frac{K}{\sqrt{H^2 - K^2}}.$$

We have therefore the relations

$$V_2 = V, \text{ and } V_3 = \frac{V}{\sqrt{1 - V^2}}.$$

It is quite immaterial which expression for V is assumed, provided this be the quantity actually measured by experiment. It has been found that the simple eye-estimates of the distinctness of the fringes coincide fairly well with the results given by the first expression.

In a subsequent paper I hope to communicate some of the more interesting results of experiments with the "wave-comparer," giving the visibility-curves for the principal lines of hydrogen, sodium, thallium, and mercury, with their probable interpretation by means of the preceding formulæ.

XXXIX. *Further Contributions to Dynamometry, or the Measurement of Power.* *By* T. H. Blakesley, *M.A.*, *M. Inst. C.E.**

NOW that the advantage of using the split dynamometer to measure power, as first proposed by me more than half a decade since, seems to be at length receiving some attention through the generalization of the method when applied to transformers, discovered independently by Prof. W. E. Ayrton and myself, it may be well to point out clearly the principles upon which such an instrument must be inserted into an electrical system to effect the measurement of a physical quantity, and the nature of the quantities which admit of such measurement.

In the first place, an exact idea must be formed of the

* Communicated by the Physical Society: read February 27, 1891.

nature of the physical quantity indicated by the reading of a dynamometer, or the angle through which the torsion-head is turned to bring the coils into a standard relative position, which is usually, but not necessarily, one in which the coils are at right angles one to the other. That position has the advantage of introducing no mutual induction in the instrument itself.

Expressed mathematically, the reading measures the quantity

$$\frac{1}{T}\int_0^T C_1 C_2 dt;$$

where C_1 and C_2 are the currents at a moment through the two coils, those currents being periodic or constant (one may be constant, the other periodic), and T being an interval of time at least equal to the least common measure of the periods, and so small that the index is not able to move appreciably in the interval T. The larger the moment of inertia of the moving coil, the greater the limit which may be allowed to T.

In the year 1885, when I first suggested sending different currents through the two coils of such an instrument, I called a reading taken under such circumstances the "force-reading," to distinguish it from an ordinary dynamometer-reading in the usual case of the currents being identical in the two coils. That name was suggested by the fact that $(\text{current})^2$ has for its structural formula in the electromagnetic system the same dimensions as force, omitting the dimension of permeability. This fact is shown in Sir W. Thomson's so-called current-balances, where $(\text{current})^2$ is made to produce equilibrium with a force.

But $(\text{current})^2$ has another more important meaning. When multiplied by resistance, it means power, and therefore by itself it means power per unit of resistance; and this is its true meaning independently of permeability. The dynamometer-reading is the *mean power* per unit of resistance.

If, therefore, we know the proper resistance to multiply the dynamometer-reading by, we shall be in possession of the value of the power; and it follows that appropriate dynamometer-readings must be of extreme value in measuring power.

It will thus be seen that if the physical quantity Z can be expressed for its momentary value in terms quadratic in the instantaneous currents, these terms will point out to us the appropriate places for dynamometers whose readings, being filled in in the places of those quadratic expressions, will give us the mean value of (Z). To make this perfectly clear:—

Suppose

$$Z = A \cdot c_1^2 + Bc_1c_2 + Cc_2^2$$

at any instant; then the mean value of Z will be

$$A \cdot {}_1D_1 + B\,{}_1D_2 + C\,{}_2D_2,$$

where ${}_1D_2$ is the reading of a dynamometer one of whose coils carries c_1 and the other c_2.

If Z is power, A, B, C are of the order resistance. If Z is $\overline{\text{E.M.F.}^2}$, A, B, C are of the order (resistance)^2. It is necessary that A, B, C should not be functions of the time. Hence power and $\overline{\text{E.M.F.}^2}$, the latter being merely power per unit of conductivity, are very appropriate quantities for the method.

To take the simple case of two machines working in parallel into a third inductionless circuit. The equations are

$$e_1 - f = r_1c_1,$$

$$e_2 - f = r_2c_2,$$

$$f = r_3c_3,$$

and

$$c_1 + c_2 = c_3\ ;$$

where e_1 and e_2 are the total E.M.F.s of the generators in the two loops 1 and 2 (including all induction); c_1, c_2, and c_3 are the three instantaneous currents, the two former positive towards the same point of junction, the latter positive towards the other, so that $c_1 + c_2 = c_3$ always; and f is the potential difference at the points where the circuits join.

Then, since

$$e_1c_1 = r_1c_1^2 + r_3c_1c_3 \text{ or } \overline{r_1 + r_3}c_1^2 + r_3c_1c_2,$$

$$e_2c_2 = r_2c_2^2 + r_3c_2c_3 \text{ or } \overline{r_2 + r_3}c_2^2 + r_3c_1c_2,$$

we have power of 1st generator

$$= r_1\,{}_1D_1 + r_3\,{}_1D_3, \text{ or } \overline{r_1 + r_3}\,{}_1D_1 + r_3\,{}_1D_2\ ;$$

power of 2nd generator

$$= r_2\,{}_2D_2 + r_3\,{}_2D_3, \text{ or } \overline{r_2 + r_3}\,{}_2D_2 + r_3\,{}_1D_2,$$

where D refers to a dynamometer-reading.

Here we appear to require four dynamometers: but the expression for the instantaneous power may be written in the 2nd form given, which necessitates only three dynamometers. Either generator here becomes a motor if the second term as

given above has changed sign, and is of greater numerical value than the first term, which is necessarily positive.

The expressions for determining the mean E.M.F.^{2} of the machines are:—

$$\left.\begin{aligned}(\text{mean } e_1^2) &= r_1^2{}_1D_1 + r_3^2{}_3D_3 + 2r_1r_3{}_1D_3,\\ (\text{mean } e_2^2) &= r_2^2{}_2D_2 + r_3^2{}_3D_3 + 2r_2r_3{}_2D_3,\end{aligned}\right\}\ \text{taking five dynamometer-readings.}$$

But this can be simplified, as in the formulæ for the powers, thus :—

$$\begin{aligned} e_1 = r_1c_1 + r_3c_3 &= \overline{r_1 + r_3}c_1 + r_3c_2,\\ e_2 = r_2c_2 + r_3c_3 &= \overline{r_2 + r_3}c_2 + r_3c_2;\\ \therefore\ e_1^2 &= \overline{r_1 + r_3}^2{}_1D_1 + r_3^2{}_2D_2 + 2\cdot\overline{r_1 + r_3}\cdot r_3{}_1D_2,\\ e_2^2 &= \overline{r_2 + r_3}^2{}_2D_2 + r_3^2{}_1D_1 + 2\cdot\overline{r_2 + r_3}\cdot r_3{}_1D_2; \end{aligned}$$

in which expressions there are only three dynamometer-readings, and these the same three as for giving the two powers.

It is clear that $-r_3c_3c_2$ is the power doing work upon the second circuit; for it is equal to $-fc_2$ at any moment; $\therefore$ $-r_3{}_2D_3$ is the mean power expended in the second circuit.

This is quite independent of the nature of the apparatus in the second circuit, which may contain any or all of the following :—

A perfect or absorbent condenser,
An electromagnet,
A decomposing-cell,
A vacuum-tube,
A motor-circuit,
A transformer-circuit,
A generating-circuit,
A welding-machine,
A tuning-fork, or other make and break.

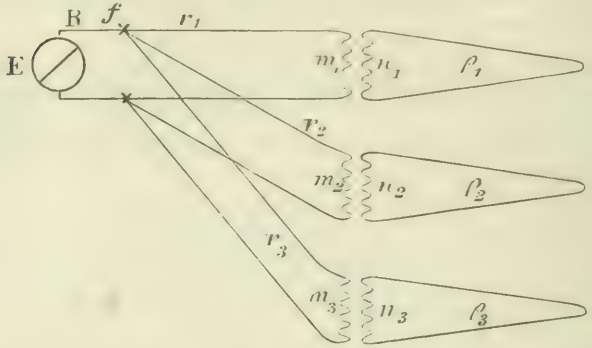
Should the apparatus render it undesirable to have the current c_2 passed through the dynamometer, we may write

$$-r_3c_3c_2 = -r_3c_3(c_3 - c_1) = r_3c_1c_3 - r_3c_3^2,$$

or $$\text{Mean Power} = r_3\{{}_1D_3 - {}_3D_3\}.$$

It was by this means that I suggested to Mr. Swinburne he might measure the dielectric hysteresis of his condensers. It would only take two dynamometers, as is seen.

The Case of a Machine playing into a Number of Parallel Transformers.



Let E be the E.M.F. of the machine (including all induction);
R its resistance;
f the P.D. where the circuits become parallel;
r the resistance of the primary from this point;
m the number of turns in the primary coil;
n the number of turns in the secondary coil;
ρ the resistance of the secondary coil.
C is the current through the generator;
c is the current in the primary;
γ is the current in the secondary;
N the number of magnetic lines in the core.

Numerical subscripts must be applied where required for the various circuits.

Then

$$\left.\begin{aligned} &E-f=CR,\\ &f-m\frac{dN}{dt}=cr,\\ &n\frac{dN}{dt}=\gamma\rho, \end{aligned}\right\}\quad\left.\begin{aligned} &\therefore\ f=cr+\frac{m}{n}\gamma\rho\ ; \end{aligned}\right\}\quad\therefore\ E=CR+cr+\frac{m}{n}\gamma\rho;$$

multiplying f by c,

$$fc=c^2r+\rho\frac{m}{n}\gamma c,$$

which gives the power in each transformer circuit, and indicates the appropriate positions of the two instruments, viz. one with both coils in the primary, and one split between the primary and the secondary.

$\rho \frac{m}{n} \gamma c$ is the power heating transformer and secondary,

$\rho\gamma^2$ is the power heating the secondary;

$\therefore \rho \frac{m}{n} \gamma c - \rho\gamma^2$ is the power heating the core, being the result of hysteresis and Foucault currents.

Multiply E by C, and we have the total power, which is

$$\mathrm{R} \cdot \mathrm{C}^2 + r\mathrm{C}c + \frac{m}{n} \rho \cdot \mathrm{C}\gamma.$$

Thus the whole power consumed in such a system may be measured by means of three dynamometers judiciously applied to the main current and those in *a single* branch.

This, of course, can be applied to measure the power at work in a system of parallel transformers by means of a home transformer, whose resistances may be kept fixed or at least accurately determined.

It may also be used to measure the electric power of a *welding* transformer, into whose secondary it is inexpedient, if not impossible, to introduce any extra resistance.

In this case a very high power would be rendered measurable by increasing the resistances in the circuits of the parallel system. The power consumed in the parallel system being, as indicated, known, can be deducted from the total.

Transformers in Series.

Let E be the E.M.F. of the machine;

r_1 be the resistance of the 1st primary;

r_2 „ „ 1st secondary and 2nd primary;

r_3 „ „ 2nd „ 3rd „

N_1 be the magnetic lines in 1st core;

N_2 „ „ 2nd „

$\left.\begin{matrix} m_1 \\ n_1 \end{matrix}\right\}$ = turns in $\left\{\begin{matrix} \text{primary} \\ \text{secondary} \end{matrix}\right\}$ of 1st transformer;

$\left.\begin{matrix} m_2 \\ n_2 \end{matrix}\right\}$ = „ „ 2nd „

c_1 = current in 1st section;

c_2 = „ 2nd „

Then

$$\mathrm{E} - m_1 \frac{d\mathrm{N}_1}{dt} = r_1 c_1;$$

$$n_1 \frac{d\mathrm{N}_1}{dt} - m_2 \frac{d\mathrm{N}_2}{dt} = r_2 c_2,$$

$$n_2 \frac{d\mathrm{N}_2}{dt} - m_3 \frac{d\mathrm{N}_3}{dt} = r_3 c_3,$$

&c., &c.

$$\therefore \quad \mathrm{E} = r_1 c_1 + \frac{m_1}{n_1} r_2 c_2 + \frac{m_1 m_2}{n_1 n_2} r_3 c_3 + \frac{m_1 m_2 m_3}{n_1 n_2 n_3} r_4 c_4 + \&c.$$

The series has $q+1$ terms when there are q transformers The square of this expression will have every term quadratic in current, and be thus amenable to dynamometer treatment.

The value for one transformer has already been given by me.

If we multiply through by c_1, we have the total power $c_1\mathrm{E}$ given in suitable terms.

For one transformer,

$$c_1\mathrm{E} = r_1 c_1^2 \quad + \frac{m}{n} r_2 c_2 c_1;$$

or power

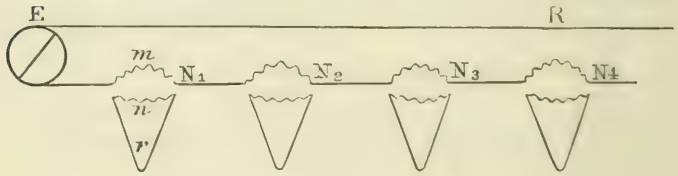
$$= r_{1\,1}\mathrm{D}_1 + \frac{m}{n} r_{2\,1}\mathrm{D}_2,$$

the first term heating the primary; $r_{2\,2}\mathrm{D}_2$ is the power heating the secondary.

Therefore the power involved in warming the core by the magnetic changes is

$$\frac{m}{n} r_{2\,1}\mathrm{D}_2 - r_{2\,2}\mathrm{D}_2 \quad = r_2 \left\{ \frac{m}{n}\,{}_1\mathrm{D}_2 - {}_2\mathrm{D}_2 \right\}.$$

The Case of Transformers with Primaries in Series.



E is the E.M.F. of the generator;
N the number of magnetic lines in the core;
m the number of turns in the primary of a transformer;
n the number of turns in the secondary of a transformer;
C the current in the primary;
R its resistance;
c the current in the secondary;
r its resistance.

Numerical subscripts being added where required.

Then

$$E - m_1 \frac{dN_1}{dt} - m_2 \frac{dN_2}{dt} - m_3 \frac{dN_3}{dt} - \&c. = CR.$$

$$n_1 \frac{dN_1}{dt} = c_1 r_1 ;$$

$$n_2 \frac{dN_2}{dt} = c_2 r_2 ;$$

$$n_3 \frac{dN_3}{dt} = c_3 r_3 ;$$

&c. &c.

$$\therefore E = CR + \frac{m_1}{n_1} c_1 r_1 + \frac{m_2}{n_2} c_2 r_2 + \frac{m_3}{n_3} c_3 r_3 + \&c.$$

The square of this will be quadratic in c, and the terms will indicate the proper places for dynamometers. The total power is

$$EC = C^2 R + r_1 \frac{m_1}{n_1} C c_1 + r_2 \frac{m_2}{n_2} C c_2 + \&c.$$

The first term heats the primary, and each succeeding term indicates the power employed in heating a secondary and a core corresponding with it. Both in this case and in the case of parallel transformers it appears that the power heating the core and its secondary is indicated by one dynamometer-reading alone, one coil being in the primary and the other in the secondary; the reading requiring multiplication by the ratio of the coil-turns in the primary to those in the secondary, and by the secondary resistance ; *i. e.* this power

$$= r_2 . \frac{m}{n}{}_1 D_2.$$

Does not this indicate the direction which efforts should take to effect a really fair mode of measuring Electrical Energy supplied?

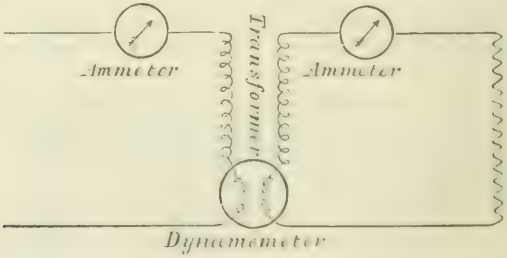
In some cases a single instrument might be used, even if the formula indicated two terms, to obtain the required measurement. Suppose, for instance, that the formula had two terms $(c_1^2 - c_1 c_2)$. This may be written $c_1(c_1 - c_2)$; and it is clear that if we had two fixed similar coils both in one plane, and made to carry c_1 and c_2 *reversed*, respectively, and if the movable coil were made to carry c_1, then the indications of the instrument would give the required measurement. It might be possible to multiply such coils, and vary their turns and position so as to meet any case, if desirable. The method is merely indicated here.

From what I have said, it will not surprise those who have followed me that in questions of power I recommend that quotations should be made of mean $\overline{\text{current}^2}$, as indicated by dynamometers, and that attempts at giving mean current in amperes, with reversing currents, should be given up. What a quantity of pains has been taken to make voltmeters give indications proportional to volts! The merit of a difference of potential is as its square, and that of cells as the square of their E.M.F. Give me twice the E.M.F., you quadruple my power of doing work by its means. To reduce readings to give the square root of mean square is doubly wrong. It is a ridiculous attempt to reach a useless quantity, and, further, gives one the trouble of squaring back again.

XL. *Proof of the Generality of certain Formulæ published for a Special Case by* Mr. Blakesley. *By* Prof. W. E. Ayrton, *F.R.S., and* J. F. Taylor*.

I.

In May 1888 Mr. Blakesley described before this Society† a very interesting method of testing the power given to the primary coil of a transformer based on the employment of three dynamometers. The method, however, really only requires two alternate current ammeters and one dynamometer with two coils. The ammeters are placed respectively in the primary and secondary circuits of the transformer, while the two coils of the dynamometer are electrically separated from one another, one being placed in the primary and the other in the secondary circuit of the transformer, as shown in the figure.



Mr. Blakesley in his paper assumed that the three instruments were not graduated directly; that is to say, that con-

* Communicated by the Physical Society: read February 27, 1891.
† Proc. Phys. Soc. ix. p. 286; Phil. Mag. [5] xxvi. p. 34.

stants had to be employed in each case to reduce the arbitrary scale-readings to absolute measure. We will, on the contrary, suppose the instruments to be graduated as they ought to be, so that if D_p, D_s, and D_{ps} be the readings of the three instruments, they are equal respectively to the square root of the mean square of the primary current, the square root of the mean square of the secondary current, and the mean product of the two currents.

With this definition Mr. Blakesley proved geometrically that the watts given to the primary coil of the transformer were equal to

$$pD_p^2 + \frac{P}{S} sD_{ps} ;$$

where p and s are the resistances, in ohms, of the primary coil and the whole secondary circuit respectively, and P and S are the numbers of windings in the primary and secondary coils of the transformer.

The formula is a simple one, and the values of the expressions in it are fairly easy to obtain experimentally. The proof of the formula, however, as given by Mr. Blakesley, was based on the following assumptions :—

1. The variations of the primary and secondary currents are harmonic.
2. The variation of the magnetism of the core is harmonic.
3. The magnetic stresses produced in the iron core by the currents in the primary and secondary coils are directly proportional to the ampere-turns in these two coils.
4. Each turn in each coil embraces at any moment the same number of lines of force.
5. The secondary circuit outside the transformer is non-inductive.

II.

In the spring of last year, 1890, Mr. Wightman, one of the third-year students of the Central Institution, showed that an analytical method for measuring the efficiency of a transformer, which had been described in one of the lectures at the college, could by a slight transformation be employed to prove the generality of Mr. Blakesley's formula given above.

The proof is quite simple, and shows that the formula in question is true whatever function the currents or the magnetism be of the time, and whatever amount of hysteresis or magnetic lag may exist. In fact the proof is independent of Mr. Blakesley's assumptions Nos. 1, 2, and 3, mentioned above.

We have delayed the publication of this proof until we had used the method for a lengthy series of experiments on a transformer kindly lent us by Mr. Mordey, and which has occupied the students for many months. But, in order that others like ourselves should be able to use Mr. Blakesley's formula with confidence, and without having any longer the fear that if the sine law were not true, or if much hysteresis existed, their calculations made by means of this formula from experimental results might be very wrong, we communicated nearly a year ago the general character of the proofs that we had arrived at to Mr. Blakesley and to others interested in the matter.

Let V_p be the P.D. in volts at the terminals of the primary-coil at any moment t.

Let A_p be the primary current, in amperes, at the same moment.

Let A_s be the secondary current, in amperes, at the same moment.

Let n be the number of lines of force passing through one convolution at that moment.

Then

$$V_p = pA_p + \frac{1}{10^8} P \frac{dn}{dt},$$

$$sA_s = \frac{1}{10^8} S \frac{dn}{dt};$$

$$\therefore \quad V_p = pA_p + \frac{P}{S} sA_s.$$

$$\therefore A_p V_p = pA_p^2 + \frac{P}{S} sA_p A_s.$$

If T be the time of one complete cycle,

$$\frac{1}{T}\int_0^T A_p V_p dt = \frac{p}{T}\int_0^T A_p^2 dt + \frac{P}{S}\frac{s}{T}\int_0^T A_p A_s dt.$$

But the expression on the left-hand side is the mean watts given to the primary coil, and the expression on the right-hand side is simply

$$pD_p^2 + \frac{P}{S} sD_{ps};$$

D_p, as already explained, being the reading of the alternate current ammeter in the primary circuit, and D_{ps} the reading

of the dynamometer having one coil in the primary and the other coil in the secondary circuit.

The following is another general proof of the same formula :—

The watts given to the primary coil of a transformer are spent partly in heating the primary coil, and partly in doing work against the back electromotive force set up by the varying magnetism of the core.

The watts spent in heating the primary coil are of course pD_p^2 ; while the watts spent in doing work against the back electromotive force are at any moment $A_p \times$ the back E.M.F.

The E.M.F. generated in the secondary circuit by the same variation of magnetism of iron is at any moment sA_s; therefore the back E.M.F. in the primary coil at the same moment must be $\frac{P}{S} sA_s$.

Consequently the total watts given to the primary coil are

$$pD_p^2 + \frac{P}{S}\frac{s}{T}\int_0^T A_p A_s dt ;$$

$$pD_p^2 + \frac{P}{S} s D_{ps}, \text{ as before.}$$

III

This expression, as Mr. Blakesley points out, may be written as follows :—

$$pD_p^2 + sD_s^2 + s\left\{\frac{P}{S} D_{ps} - D_s^2\right\} ;$$

and since $pD_p^2 + sD_s^2$ are the watts employed in heating the primary coil and the whole of the secondary circuit, it follows that

$$s\left\{\frac{P}{S} D_{ps} - D_s^2\right\}$$

are the watts employed in heating the core on account of hysteresis or magnetic lag ; a result now proved true independently of all assumptions as regards the sine law, or the magnetic stress being directly proportional to the ampere-turns, &c.

IV.

Since the portion of the secondary circuit outside the transformer is non-inductive and has a resistance s' say, the watts

developed in it are of course $s'D_s^2$. Consequently the efficiency of the transformer is

$$\frac{s'D_s^2}{pD_p^2 + \frac{P}{S} sD_{ps}}.$$

V.

Using the various assumptions already referred to, Mr. Blakesley arrived, by means of a geometrical proof, at a formula for measuring the mean square of the P.D. at the terminals of the primary coil by means of the two ammeters and the dynamometer.

The following *general* proof of this formula is very much simpler than the proof for only a special case which Mr. Blakesley gives, and furnishes a very good example of the fact that sometimes it is more easy to give an analytical proof which is true independently of any assumptions about the harmonic law, &c. than to give a geometrical proof which is only true when these suppositions hold.

$$V_p = pA_p + \text{the back E.M.F. at the moment}$$

$$= pA_p + \frac{P}{S} sA_s ;$$

$$\therefore \frac{1}{T}\int_0^T V_p^2 dt = \frac{p^2}{T}\int_0^T A_p^2 dt + \frac{P^2 s^2}{S^2 T}\int_0^T A_s^2 dt + 2\frac{P}{S}\frac{ps}{T}\int_0^T A_p A_s dt ;$$

that is, the mean square of the P.D. at the terminals of the primary coil equals

$$p^2 D_p^2 + \frac{P^2}{S^2} s^2 D_s^2 + 2\frac{P}{S} ps D_{ps},$$

which is the formula given by Mr. Blakesley.

From the preceding it follows that Mr. Blakesley's expressions for the watts given to the primary coil of a transformer, for the efficiency of the transformer, and for the mean square of the P.D. at the terminals of the primary coil, are true irrespectively of any assumptions as to the functions the E.M.F.s, the currents, or the magnetic flux are of the time as well as of any assumptions as to the presence or absence of hysteresis or magnetic lag.

This being the case, the application of this two ammeters and dynamometer method for measuring power in other cases than those already treated of is worthy of careful consideration.

XLI. *On Relations between the Lines of various Spectra.* *By* W. N. Hartley, *F.R.S., Professor of Chemistry, Royal College of Science, Dublin.*

IN a paper published in the Philosophical Magazine for July 1890 (vol. xxx. p. 33), by Mr. J. S. Ames, "On Relations between the Lines of various Spectra, with special Reference to those of Cadmium and Zinc, and a Redetermination of their Wave-lengths," the author refers to two of my papers, the titles of which follow :—"Notes on certain Photographs of the Ultra-violet Spectra of Elementary Bodies," J. Chem. Soc. vol. xli. p. 84, 1882 ; and "On Homologous Spectra," *loc. cit.* vol. xliii. p. 390, 1883. The substance of these papers may be stated in a few words.

I observed a remarkable likeness between the individual lines in the spectra of different elements belonging to the same group, but striking differences between the characters of the lines belonging to elements of different groups. The spectra of the alkali metals were quite different from those of the magnesium group. These latter differed from the iron group. The aluminium, indium, thallium spectra differed from any of the others. The metalloids tellurium, arsenic, and antimony had distinct characters in common. The differences in the lines of various spectra observed were, first in intensity of chemical action, secondly in length, thirdly in extension above and below the points of the electrodes, and fourthly in breadth or shape, as, for instance, with or without a nimbus. These physical characters were first described by me in the Scientific Transactions of the Royal Dublin Society, vol. i. p. 231, 1881. So important were they considered, that a large amount of labour was incurred in giving a minute description to each line in the tables of wave-length measurements made by Mr. Adeney and myself (Phil. Trans. vol. clxxv. p. 63, 1884). Only two other observers have given particular descriptions of the physical characters of lines in spectra, namely, Messrs. Thalén and Lecoq de Boisbaudran. A community of characteristics in spectra was recognized as being due to a similarity in the properties of elements belonging to the same group when classified according to the Periodic Law. Elements with properties in common likewise exhibit spectra with similar groupings of lines ; but the dispersion of the lines and the refrangibility of the strong lines in each group vary with the atomic mass of the elements. The

* Communicated by the Author.

communications in which these matters were dealt with were illustrated by photographs of spectra enlarged to 36 × 28 inches. In the group of metals comprising magnesium, zinc, cadmium, each spectrum consists of (1) single lines, (2) pairs of lines, (3) a series of triplets, (4) a quadruple group, and (5) a quintuple group. When oscillation-frequencies are calculated from the wave-lengths of the lines in each spectrum, the differences between the oscillation-frequencies in each triplet in any one series is a constant quantity; the law applies also to the series of doublets. The differences between the oscillation-frequencies of individual rays in the series of triplets increases with the atomic mass of the elements to which the triplets belong.

A survey of the facts led me to the conclusion that these elements are composed of the same kind of matter in different states of condensation, the molecules having similar modes, but different rates of vibration. This law of homology in spectra has been elaborately studied by J. R. Rydberg, who it appears recognized it independently in 1885 *.

The spectra studied by me were spark-spectra, and concerning this point Mr. Ames writes:—"But it is hardly safe to draw inferences from spark-spectra; for, although they are undoubtedly characteristic, yet the state of affairs in the spark-discharge is so unnatural, if I may use the term, that similar molecules could not be expected to act alike." There are, of course, good reasons for studying both arc- and spark-spectra and there are certain features in the latter which render them of particular interest; for instance, their physical characters are more strongly marked than those of arc-spectra, their lines are sharper and very seldom diffuse as in the arc, and the same element frequently gives lines common to both arc and spark. The disadvantage is that they are more complicated. But there does not appear to be any definite reason for rejecting observations made upon spark-spectra, or regarding the inferences drawn therefrom as unsatisfactory. The conditions which are not specified, but which are referred to as influencing the mode of vibration of the molecules in vapours resulting from the spark-discharge, have never varied the spectrum of any of the metals which have come under my observation. The only element which has exhibited variations in its spectrum within my experience, is carbon in the form of graphite. This substance has been observed to yield a spectrum from which some of the lines belonging to carbon

* "Recherches sur la Constitution des spectres d'emission des éléments Chimiques." *Kongl. Svenska Vetenskaps-akademiens Handlingar*: Stockholm, Bandet 23, No. 4, 1890.

with wave-lengths 4266·3, 3919·5, 3881·9, 3875·7, 3870·7, 3590, 3585, 3583·5, 2746·6, and 2640 are absent without any apparent reason. The first five of these lines are much lengthened and strengthened when carbon dioxide is the atmosphere surrounding the electrodes and are unquestionably carbon lines (Phil. Trans. vol. clxxv. p. 49, 1884). The spectra of magnesium, zinc, and cadmium have been photographed repeatedly, and that of cadmium has been observed by me many thousands of times during the last twelve years, yet not only have the spectra been always characteristic, *but they have never varied in any single particular.*

I should infer from this that molecules of the same metal always act alike under the influence of a properly regulated spark-discharge, in spite of the fact that the motion of the spark is oscillatory. Mr. Ames further remarks :—" It is to be regretted, too, that in general so little attention has been paid to the physical properties of the lines, when homologous groups or series were selected. It is only, I think, by means of the physical similarities that correct inferences can be made. For these two reasons a great many of the relations given by Professor Hartley are inaccurate."

Nothing but the physical similarities of the lines, and their evident arrangement in pairs and triplets in the three spectra above mentioned, led to my calculations and the discovery of those relations in spark-spectra which have been recently observed by Mr. Ames in the arc-spectra of zinc and cadmium. It was therefore at least seven years prior to the publication of his paper that the importance of taking into account the physical similarities of lines and groups of lines was fully recognized.

Mr. Ames at another point in his communication makes the following statement :—" The resemblance of the spectrum of magnesium to those of zinc and cadmium is much less marked than the one just noted. In fact, I think nearly all the points of similarity given by Professor Hartley are wrong. Magnesium has, it is true, the groups of triplets ; but their physical properties bear no apparent relation to those of the zinc and cadmium triplets. The beautiful series of five lines at wave-length 2779·9 in the magnesium spectrum surely has no companions in the zinc and cadmium spectra. There is, however, one striking feature common to all three. This is the presence of one broad reversed line. In magnesium it is at wave-length 2852·2 ; in zinc, at wave-length 2138·3 ; in cadmium, at wave-length 2288·1." I do not agree with Mr. Ames, and think he is not justified in stating the opinion which is the second sentence in the foregoing quotation. The

photographic enlargements show that the magnesium triplets are the same in character as those of zinc and cadmium. First, the lines are continuous ; secondly, they have a large nimbus; thirdly, they are extended ; and, fourthly, the first and second lines in each triplet are stronger than the third, which is the most refrangible. There is, however, a difference in the first and second strong lines of the principal triplet in cadmium, and this difference is common both to my spectrum and that of Mr. Ames ; namely, the lines are double.

He suggests the probability of the corresponding zinc lines being resolvable into doublets, and I should feel inclined to suggest that in such an event the corresponding magnesium lines are with equal probability doublets. But on the whole I do not think the zinc lines are double, as it rather appears to me that we must expect certain variations in the lines of homologous spectra, and one of these is a splitting of strong lines into two in the case of elements with greatly increased atomic mass, just as the intervals between lines in the doublets and triplets in different spectra become greater with a definitely increased quantity of matter in the atoms. Of course, under such a condition, lines with approximately the same wave-length in one spectrum, and appearing as one line, would be represented by corresponding lines in the spectrum of an element of the same group, but with a higher atomic mass, as two separate lines. The individual members of any homologous series of organic substances possess certain peculiar properties which are variations from those belonging to the general type ; this is particularly the case with those terms of the series of high molecular weight, and elements of the same group exhibit properties which are still wider variations from the general properties ; therefore, in such a matter as the constitution of spectra it would indeed be strange if the latitude in such variations were not still greater. For, as the properties which the elements of the same group possess in common are fewer in number than those held in common by homologous series of organic substances, the constitution of the spectra may be expected to be less strictly defined. In other words, the spectrum of an element may be conceived as being the expression of the vibrations which are caused by all the molecular movements upon which the properties of the molecules depend.

With regard to the nine most refrangible lines in magnesium, zinc, and cadmium, I can affirm that in each spectrum they form a very striking group, particularly so in magnesium and zinc.

Of the groups comprising the first four of the nine lines in

each spectrum the exact similarity in constitution is doubtful, and this I have attributed more to inaccuracies in the measurements in this part of the zinc and cadmium spectra than to any differences in physical characters of the lines. As far as recorded observations show, the last group of five lines appear to be homologous in the three spectra. They are all continuous lines, sharp, and only slightly extended, but exhibiting certain differences which might be accounted for by the atomic mass of the elements being different

It may be remarked that Mr. Ames appears to have worked only with arc-spectra, and that he has had the advantage of using a Rowland concave grating of great power; notwithstanding the amount of dispersion at command, the lines which he describes as single are single in my spectra, and those which he finds to be double are also described as such by me. In fact, by the use of prisms for photographing, and a magnifying power of from 25 to 50 diameters for examining the photographs, an extraordinary dispersion in the ultra-violet is easily obtained. There are some advantages in the use of prism-spectra, first, because there is very little loss of light and the exposure is not unduly prolonged; secondly, the distinctive features of the lines are much more pronounced.

The study of homologous spectra I believe will lead to an elucidation of the constitution of the chemical elements; but before this field of inquiry can be made highly productive there is need for a revision of the wave-lengths of some of the extreme rays in the ultra-violet spectra, and we require also a means of photographing with facility from wave-lengths 2000 to 1800 or further.

XLII. *Notices respecting New Books.*

A Short Course of Experiments in Physical Measurement. By Harold Whiting, *Instructor in Physics at Harvard University.* Part II.: *Sound, Dynamics, Magnetism, and Electricity.* (Cambridge, Massachusetts: John Wilson & Son.)

THE volume before us is issued as the second part of an elementary treatise on practical physical measurements, of which the first part was published about a year ago, and has previously been noticed in this Magazine. A hope was then expressed that the figures and pictures of apparatus would be improved in the succeeding volumes, but we regret that this hope has not been realized. On opening the book we are immediately confronted by some of the worst woodcuts which we ever remember to have seen in any scientific work. In the case of simple diagrams, where there are no shaded parts, the figures are

intelligible and in some cases fairly good, but wherever any shading has been attempted the detail is entirely obscured and the figure rendered almost or quite worthless. As examples of this, the diagrams of the pulley-blocks (p. 379) and of the speed-counter (p. 535) may be mentioned, though these are not chosen as being conspicuously bad. In other cases the figure is spoiled by a too great similarity between different parts of the apparatus, as in the ammeter (p. 466), where the coil conveying the current and the controlling horseshoe permanent magnet are drawn so as to look exactly like two parallel coils; or, again, in the sketch of Poggendorff's method of comparing electromotive forces (p. 531), in which the traditional diagram has been departed from, and a very remarkable series of circles put in its place.

It is to be regretted that the work of the engraver has been so badly executed, since the book is on this account debarred in a great measure from use by any except those who have access to the actual apparatus described (presumably that of Harvard University). The text and the order in which the experiments are given are both good, and maintain the standard of the first volume. We find in many experiments special devices referred to which should materially help to increase the degree of accuracy obtainable. As an instance we may mention the use of the micrometer-screw to measure the amount of bending of a loaded beam; the point of the screw touching the beam closes an electric circuit and rings a bell. Some few omissions have, as we think, been made; nothing is said, for example, about the water voltameter, although the direct comparison of the electrochemical equivalents of, say, copper and hydrogen, is a very easy, satisfactory, and instructive experiment, the results of which are independent both of the constancy of the current used and of its duration. Moreover, the experiment affords a good example of the correction of the volume of a gas for temperature and pressure.

In our perusal of the book we have noted one or two misprints in the text, which will scarcely lead to mistakes or confusion, except, perhaps, in the description of experiment 98, where Leclanché is spelt Lechanché throughout. A dash is omitted in each of the formulæ (5) and (6), p. 441, and in the lower formula of page 563 the d should be t in order to accord with a previous formula there referred to.

James L. Howard.

The Steam-Engine considered as a Thermodynamic Machine: a Treatise on the Thermodynamic Efficiency of Steam-Engines, illustrated by diagrams, tables, and examples from practice. By J. H. Cotterill, *F.R.S.* (London: E. & F. N. Spon, 1890. Pp. xi +426.)

The first edition of this work was published in December 1877, and was intended "to serve as an introduction to applied thermodynamics, while at the same time an attempt was made to study,

more completely than had hitherto been done, the process of the conversion of heat into work in steam-engines." The treatise has been long out of print, and so, with a diffidence it is hard to understand, the author has brought out the present edition. This reluctance, however, is due to the thought that so great progress has been made since 1877, that some might wish that a new work had been written rather than a new edition of an old one published. The present volume contains eleven chapters, accompanied by sets of useful Tables, and followed by an appendix containing Notes and Addenda. The first nine chapters in the main are a reprint, but numerous additions and improvements have been made in them to bring the work up to date. These additions are more especially indicated in the Appendix. For the benefit of such as have not a copy of the work, we briefly note the subjects discussed in these chapters. The first treats of the physical properties of steam, the author then coming to thermodynamics, discusses the convertibility of heat and work, and treats of the formation of steam in a closed vessel, and of internal work in general. Chapters 3, 4, and 5 are taken up with a preliminary theory of the Steam-Engine, an account of Air- and Gas-Engines, statement of the Second Law of Thermodynamics, an enunciation and explanation of Carnot's principle, and accounts of some perfect Thermodynamic Machines. Chapter 6 is devoted to the generation and expansion of Steam. In Chapter 7 we have extensions of Carnot's principle, of the adiabatic equation (with numerical examples), and the connexion between adiabatic curves, with a discussion of several other matters bearing upon the subject of perfect engines with any given cycle. The losses of efficiency in Heat-Engines occupy chapter 8, and clearance and wire-drawing form the subject-matter of chapter 9. The last two chapters have been completely rewritten; this is in consequence of the attention which has of late years been paid to this branch of the subject, viz., the action of the sides of the cylinder and of water remaining after exhaust, and the conditions of economical working of Steam-Engines. They occupy one quarter of the book, and contain much matter of interest. If the statements made in this concluding part meet with acceptance, and some little time must elapse before a sufficient trial can be made of them, then the author's success will be as great as it was upon the appearance of the first edition. Every one must wish that "the not inconsiderable amount of time and labour which has been spent in its preparation" by one whose time is well occupied with regular professorial work, may meet with an ample reward. The book is elegantly got up, and, notwithstanding the early clerical error (p. iv) of "then" for "than," is, we think, printed with extreme accuracy.

XLIII. *Intelligence and Miscellaneous Articles.*

ON THE REFLEXION OF RAYS OF ELECTRICAL FORCE FROM PLATES OF METAL AND OF SULPHUR. BY PROF. KLEMENČIČ, IN GRATZ.

THE author has undertaken to investigate the reflexion of the rays of electrical force at a dielectric plate of sulphur and at a zinc plate, both qualitatively and quantitatively; and to compare also in this respect the behaviour of these rays with those of light.

In investigating the rays, he used secondary inductors with interposed thermopile, as has been already described in a previous paper (Phil. Mag. vol. xxx. p. 284). Two inductors were used this time—the one as a standard, the other as the proper movable secondary inductor.

The reflexion took place against a sulphur plate, the dimensions of which were 120 centim. by 80 by 7, and which was made up of twelve bricks; the dimensions of the zinc plate were the same except in the matter of thickness, which was far less. In addition to this, the author investigated the portion of the rays transmitted by the plates. The experiments on the reflexion of metals were completed by observations on a wire grating, and on a round zinc plate. The dimensions of the reflecting-plate and of the mirror permitted the investigation only of the incident angles 30° and 65°.

Between the reflexion at the zinc plate and that of the sulphur plate, it has been found that there was a difference, which qualitatively corresponds to the deportment of the rays of light. The intensity of the reflexion is different according to the direction of vibration of the rays. With the sulphur plate there is a powerful reflexion under all angles of incidence, if the vibrations are at right angles to the plane of incidence. It is otherwise with rays in which the vibrations are parallel to the plane of incidence. In this case a faint reflexion is found only with small angles of incidence; the intensity of the same increases with increasing angle of incidence; and at 60° to 65° no perceptible reflexion could be established with the methods here employed. This fact agrees very well with the optical relations, in so far that from the refractive indices of sulphur there is, in fact, a polarizing angle of between 60° and 65°. As regards the question of the direction of vibration in polarized light, the conclusions which result from these experiments are the same as those found by Troughton ('Nature,' xxxix. p. 391). It was further observed that the intensity of the ray transmitted by the sulphur plate was the opposite of that of reflexion.

Although for individual angles of incidence the results obtained by calculations with Fresnel's formula for intensity are in good agreement, yet, in general, this does not hold. Some remarkable phenomena occur which do not harmonize with the behaviour of

rays of light, which have probably their origin in the fact that the dimensions of the reflecting ray are too small in comparison with the wave-length of the ray.— *Wiener Berichte*, Feb. 19, 1891.

ON THE OPTICAL PROPERTIES OF α-MONOBROMONAPHTHALINE.

BY B. WALTER.

It frequently occurs in researches on fluorescence, phosphorence, &c., that the well-known powerfully dispersive media prisms of flint glass and of carbon bisulphide cannot be used, because they completely extinguish the ultra-violet portion of the spectrum. It is therefore of interest to direct attention to the remarkable property of α-monobromonaphthaline, which, in addition to its great dispersive power, has also a *remarkably complete transparency for ultra-violet rays*. For instance, I caused the spectrum produced by a hollow prism filled with this material to fall on a trough containing solution of æsculine, and I could observe the solar spectrum in the ultra-violet beyond N. That the absorption which occurred from this point was not caused by the monobromonaphthaline, but by the various glasses which I had to use, follows from the fact that the spectrum was the same whether I allowed the rays to pass near the base or near the apex of the prism. By comparing photographs of diffraction-spectra with those of monobromonaphthaline, I am convinced that the absorption of ordinary crown glass extends just into those regions.

If, in addition to these properties of great dispersion and transmissibility for ultra-violet, we remember that its boiling-point is at 277° C., that it has not the objectionable smell of carbon bisulphide, and that its refractive index for each degree Centigrade only increases by $0{\cdot}0_3 48$ instead of $0{\cdot}0_3 80$ with carbon bisulphide, we shall see that optical science has a very valuable acquisition in this substance. It is said that it alters somewhat with time; but this cannot be very considerable, as the liquid in my possession has still the same properties without alteration as at first. My determinations also of the refractive indices agree very well with the individual statements of the older observers (Fock and Pulfrich); but they differ from those of Dufet (*Journal de Physique* [2] iv. p. 415, 1885), although both preparations proceed from the same source.

Refractive indices of α-monobromonaphthaline at 20° C.:—

A.	a.	B.	C.	D.	E.
1·64051	1·64367	1·64638	1·64948	1·65820	1·67049

F.	H_γ.	G.	Hδ.	H.
1·68195	1·70410	1·70595	1·71855	1·72893.

The letters refer generally to Fraunhofer's lines, excepting H_γ and Hδ, which denote hydrogen-lines. The refractive index of the D line decreases $0{\cdot}0_3 48$ for 1°. The density of my monobromo-

naphthaline amounts to 1·4916 at 20°, and decreases $0{\cdot}0_3 70$ for 1° C. The preparation was obtained from Dr. Schuchardt in Görlitz.—Wiedemann's *Annalen*, No. 3, 1891.

ON THE LINE SPECTRA OF THE ELEMENTS OF MENDELEJEFF'S SECOND GROUP. BY PROF. KAYSER AND PROF. RUNGE.

After we had examined the spectra of the elements of Mendelejeff's first group, and had found that they were built up entirely in accordance with law, we passed to the elements of the second group, with the exclusion of beryllium. Here also we have succeeded in finding an entirely homologous structure of the spectra; while for the alkalies, pairs of lines were characteristic which either showed variable difference of vibration (principal series) or constant difference of vibration (secondary series), the elements of the second group are characterized by triplets of lines. Each element has constant differences of vibration ν_1 and ν_2 both between the first and second and second and third line of all triplets. Of the triplets of each element, one portion is stronger and less sharp; they form a series of triplets the lines of which can be represented with great accuracy by the equation which we used with the alkalies,

$$\lambda^{-1} = A - B_n^{-2} - C_n^{-4}.$$

We call those the first *secondary series*. The other triplets are fainter, but sharper, broadened only on the side of the longer waves. They also form a series, our second *secondary series*. For Mg, Ca, Zn, Cd, Hg, we have found the first and second series, for Sn only the first, while for Ba we have not been able to find any series.

According to their spectra the elements fall into two divisions—Mg, Ca, Sr, and Zn, Cd, Hg; the latter three more especially present various common phenomena on which this is not the place to enter. In each division, with increase of atomic weight the series move towards the side of the longer waves, as is also the case with the alkalies. In this, however, the second division is displaced towards the side of the shorter waves.

While all lines of the spectrum were taken up by the series in the case of the alkalies, in the present case this is not so: about half the lines observed are superfluous in each spectrum. For a number of them we have also found regularities, since they form either pairs with definite distances or triplets; in any case the number of lines which are apparently distributed over the spectrum without any regularity is a tolerably large one.

The regular displacement of a spectrum from one element to another finds a natural expression in a regular variation of the constants of our formula.—*Berliner Berichte*, Feb. 19, 1891.

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XLIV. *On the Mutual Solubility of Salts in Water.*—Part I.

By W. W. J. NICOL, *M.A., D.Sc., F.R.S.E., F.I.C., Lecturer on Chemistry, Mason College, Birmingham**.

[Plate VIII.]

IT has long been well known that certain salts exercise a marked influence on the solubility of others, when the two are simultaneously dissolved in water to saturation. In some cases the amount dissolved of both salts is greatly increased, in others as markedly diminished, while in other instances one of the salts has its solubility greatly affected while that of the other is either unaltered or changed in the opposite direction. The whole of these phenomena may be conveniently grouped under the heading, "The Mutual Solubility of Salts," which forms the title of this communication; but it is obvious that some limitation must be made, otherwise it would include cases where chemical decomposition might take place attended by precipitation. Though these are clearly inadmissible, there are other instances which would at first sight appear to come under the title, but will on reflection be found to be similar to the above. Thus all cases where rearrangement of the constituents of the salts is possible must be at present excluded; for our knowledge of the nature of solution does not enable us to say what happens when two salts MR and M′R′ are simultaneously dissolved in water: we do know that the solution is identical with that formed by

* Communicated by the Author.

dissolving M'R and MR', but we cannot tell which pair of the four possible salts is present, nor indeed can we decide definitely that all four salts are not formed in the solution. Again, cases where the salt expelled from solution by the addition of another salt is a well-defined double salt must also be excluded : for example, the separation of alum from a solution of aluminium sulphate by the addition of potassium sulphate ; for here we no longer have to deal with only two salts but with three, the third being formed by the union of the original pair, but whether this union has taken place in the solution or only at the moment of separation we cannot tell. This objection also holds good with regard to the well-defined double salts which are more soluble than one or both of their constituents, such as $HgCl_2 2NH_4Cl$; here too there may be three salts present in the solution. In all these instances, in addition to the objections already stated, there is the further fatal one, that the composition of the resulting solution is dependent on the mass of the undissolved salt.

The subject is therefore restricted to the case of isomorphous salts which crystallize together in any proportion, and to those salts which, though not isomorphous, do not form double salts. As yet I have examined the behaviour only of those salts which do not form mixed crystals.

Very numerous and careful experiments have already been made on this subject from one standpoint. Kopp, Karsten, Mulder, and Rüdorff have determined the amount dissolved of each member of a pair of salts when water is treated with excess of both salts simultaneously. The work of Kopp*, who, so far as I am aware, was the first systematic investigator in this branch of solution, for we may pass over the few experiments of Vauquelin†, led him to two main conclusions as to the behaviour of salts, when simultaneously dissolved in water to saturation. Kopp found that the salts examined by him fell into one or other of the following classes :—

1. *Salts with the same metal but with different acid radicals.*— In this case neither of the salts ever retains the same solubility as in pure water, each salt affects the solubility of the other : as a rule the amount dissolved of one of the salts is increased, while that of the other is diminished.

2. *Two salts of different metals but the same acid radical.*— "Here the rule holds that, provided there is no chemical action of the salts on one another, the salt with the stronger base retains its own special solubility, exactly as if the other

* *Ann. der Chemie und Pharm.* vol. xxxiv. (1840).
† *Ann. de Chim.* xiii. p. 86 (1792).

were not present, and this last dissolves in the solution of the first in proportions which cannot be determined *à priori*."

Kopp found some exceptions to this rule, but believed that in these cases double salts were formed which were capable of existence only in solution, being decomposed on removal of the solvent; and pointed out that in this respect as in many others sodium behaves quite differently from potassium.

This second law of Kopp breaks down completely when extended to any large number of salts, as will be seen by an examination of the Table of results of other experimenters given by me in a previous paper*.

Next in order of time come the experiments of Karsten †, who performed numerous experiments on this subject and arrived at the following conclusions with regard to the mutual solubility of salts in the restricted sense mentioned above.

1. The salt A precipitates a portion of the salt B from its saturated solution, but this is also conversely true, so that for any given temperature the proportions of A and B are constant. This Karsten calls "Die Auflösung mit wechselseitiger Absonderung."

2. The salt A precipitates a portion of B from its saturated solution until the quantity dissolved of A is the same as in a saturated solution of that salt alone; on the contrary, the addition of B does not precipitate A from its saturated solution. "Die Auflösung mit einseitiger Absonderung" (Kopp's second Rule).

3. The salt A dissolves in the saturated solution of B, and the salt B in the saturated solution of A, and no precipitation takes place. "Die Auflösung ohne Absonderung." With the salts belonging to this class, three different saturated solutions exist, formed as follows:—

(*a*) Excess of A added to saturated solution of B.

(*b*) Excess of B added to saturated solution of A.

(*c*) Excess of A and B added to water.

The somewhat cumbrous classification of Karsten resolves itself on reflection into:—

(1) The solubility of both salts is diminished.

(2) The solubility of one salt is unaffected, that of the other diminished.

(3) The solubility of both salts is increased.

The next important researches on this subject are those of Mulder‡, who in 1864 published a monograph on solution

* Phil. Mag. 1884, xvii. p. 537.

† *Ann. der Chem. und Pharm.* xl. p. 197.

‡ *Bijdragen tot de Geschiedenis van het Scheikundig gebonden Water*, Rotterdam, 1864.

which is of the greatest possible interest and importance. In it he not only gives the results and conclusions from his own experiments, but has incorporated the work of all previous experimenters. He worked with a very large number of salts, his experimental skill and accuracy are of the highest order, and, as a rule, his results are completely to be depended on, not by any means a common thing in researches on solution. I need not therefore apologize for devoting some considerable space to an examination of his results.

Mulder states, as the results of his experiments, that he knows of no better classification of salts, so far as their mutual solubility is concerned, than into the three following divisions:—

(1) Salts the amounts of which in a saturated solution are dependent entirely on the nature of the solid salts.

(2) Salts the saturated solutions of which are dependent on the affinity of the respective salts for water.

(3) Salts which resemble those in both of the foregoing classes, and consequently behave now in one way and now in another according to the amount of either salt present.

(1) Solutions of salts belonging to this class contain, when saturated, according to Mulder, the constituent salts in simple equivalent proportions, and the saturated solution has the same composition whether it is prepared by adding salt A to a saturated solution of B, or *vice versâ*, or by adding both salts in excess to water.

(2) This second class of salts is divided into two subclasses:—

(*a*) The solubility is dependent on that of one of the salts.

In this case we have to deal, according to Mulder, with double salts in solution, one of the constituents of which behaves as if it were the only salt present, dissolving in the water as if it were alone and yet permitting of the solution of a quantity of the other salt, with the result that the salts are present in a simple molecular proportion.

(*b*) The solubility is dependent on that of both salts.

We have here the remarkable fact that in a saturated solution of one salt another may be dissolved, and that to the same extent as in pure water, while the solubility of the first salt also remains unaffected. In this case also the salts are present in simple molecular proportions.

Mulder lays great stress on the existence of this simple molecular relation between the salts present in a saturated solution, and sees in it clear proof of the existence of double salts in solution and of the chemical nature of solution in

general. He has not, however, succeeded in obtaining a single one of these double salts in the solid form and in definite crystals; and it will be found, on comparing his results with those of Rüdorff, that the difference of a few degrees in the temperature of experiment is sufficient to effect a radical change in the proportions of the two salts, an effect which is extremely improbable if such double salts really existed in solution. Mulder's double salts, in all probability, owe their supposed existence to the arithmetical possibility of fitting *any* experimental ratio very closely by ratios such as 1:2, 2:3, 3:4, 4:5, &c.

Rüdorff*, the latest experimenter on the mutual solubility of salts when dissolved to saturation, has performed an immense number of very careful and exhaustive experiments not only with salts between which chemical action is impossible, but also with those where double decomposition may take place. We are here concerned only with the former. He found that these divide themselves into two groups. With some salt mixtures, as for instance nitrate and chloride of ammonium, we obtain always one and the same saturated solution, if only an excess of both salts be employed, no matter in what relative proportions the excess of both salts is brought in contact with the water. With other salts, however, such as ammonium and potassium nitrates, the composition of the resulting solution is dependent on the proportions in which the two salts are presented to the water, which is insufficient to completely dissolve either of them. An excess of the one drives out a definite amount of the other salt, so that it is not possible with these salts to prepare a saturated solution on which one or other of the salts is without action.

In his later paper on the same subject, he extends his experiments to many other pairs of salts, with the general result that, so far as we are here concerned, it is only those salts which are not isomorphous nor form double salts, nor form mixed crystals, that are capable of forming definite saturated solutions—solutions, the composition of which is unaffected by the addition of either of the salts in the solid state. A fuller account of Rüdorff's later work has already been given by me in a paper on the "Saturation of Salt Solutions."

The work of the other experimenters on this subject does not call for any special comment, as the greater part of it refers to individual cases, and is not sufficiently extended either in its aim or execution to allow of any generalization being made from it.

Though so much has been done by the four investigators

* Wiedemann's *Annalen*, xxv. p. 626.

mentioned above in their endeavour to ascertain the laws of mutual solubility of salts, it does not seem to have occurred to any one that only one, and that the least promising side of the question, had been attacked. With the exception of a few incidental experiments of Rüdorff, the attention of chemists has always been directed to the saturated solutions of both salts; no one has realized the importance of experiments on the solubility of a salt in a non-saturated solution of another; and yet a moment's thought will suffice to convince one that it is in this way, and in this way only, that the problem of mutual solubility can be solved. The influence of a salt on the solubility of another cannot possibly be studied, if only one determination be made of the condition of equilibrium in the system of two salts and water. No matter how frequently or how accurately this one determination is made, it will throw no light on the question under examination. Several years ago, soon after the publication of my previous paper on the subject, I was struck with the futility of the methods hitherto adopted, and commenced a series of experiments on an entirely fresh field of investigation; the progress of this work has been reported on from time to time to the British Association for the Advancement of Science by the Committee "On the Nature of Solution," of which I have the honour to be Secretary.

The work had for its object the determination of the solubility of one member of a pair of salts in solutions of various strengths of the other member, and *vice versâ*. In this way it was hoped that the series of experiments on solutions of gradually increasing strengths would throw light on the action of the one salt on the solubility of the other, and thus lead to a full knowledge of the condition of equilibrium in the saturated solution of both salts. How far this hope has been fulfilled will be seen below.

The course of experiment was as follows:—

A salt was taken, and solutions containing 1, 2, &c. gramme-molecules of this salt in 100 gramme-molecules of water were prepared. These solutions were then saturated at a definite temperature with the other salt added in excess, and the total salt in solution determined; precisely similar determinations were made with definite molecular solutions of the other salt. The solubility of each salt separately in water at that temperature was then determined, and, finally, the solubility of both salts when simultaneously added in excess to water was also ascertained.

The first difficulty met with was that of ensuring saturation; for the conditions of experiment necessitated the greatest care

that the water present should not be lost by evaporation, otherwise the composition of the solvent solution would be altered. The thoroughly efficient method of mixture, by blowing air through the solution, previously employed by me, could not therefore be applied. Recourse was therefore had at first to what may be termed saturation by gravitation. Tubes of the form shown in fig. 1, Pl. VIII., were made, and were used in the following manner. The bend *a* of the capillary-tube was filled with mercury. The solvent solution was poured in till it just covered the surface of the platinum gauze *b*. The salt, previously fused and cast into thin sticks, was then placed on the gauze and the open end of the tube closed with a cork. The whole was then placed in a wide test-tube, which was also corked and placed up to the mouth in the water of a bath, kept at the constant temperature of 20° C. by the method previously described by me. After the lapse of twenty-four hours the saturation-tube was quickly withdrawn. The mercury was expelled by blowing into the open end ; and in the same way a portion of the saturated solution was transferred to a weighed nickel crucible, and the amount of salt dissolved was determined in the usual way.

The above method yielded excellent results, but was somewhat troublesome, and was after a time discarded for one which did not require fusion of the salts employed. In a constant-temperature bath similar to the previous one was placed a copper water-wheel, to the axle of which were attached clips to receive the saturation-tubes. The wheel was caused to revolve by means of a current of air entering at the bottom of the bath below the inverted buckets of the wheel. The revolution of the wheel caused such a circulation of the water in the bath, that the temperature at all parts was the same, and never varied more than $\pm 0°{\cdot}02$ C. from 20° C. The wheel revolved, on an average, 18 times a minute, or 1000 revolutions per hour ; and as saturation extended over a period of 20 to 24 hours, the salt and solvent solution contained in the saturation-tubes attached to the axle of the wheel were shaken together 20,000 to 24,000 times. The solvent solution and the salt in excess were placed in narrow test-tubes closed with rubber stoppers, and enclosed in wider tubes, also closed, and placed in the clips on the axle. After saturation had gone on for the required time, the tubes were removed from the wheel and placed in an upright position in the bath, and, when the excess of salt had settled down, leaving the solution perfectly bright and clear, a portion was quickly decanted into nickel crucibles and estimated in the usual way. In every case two or more determinations were made.

The salts hitherto examined are not very numerous, but are typical examples of two important classes, the chlorides and nitrates. Indeed, it was found that only a limited number of salts were available for this form of experiment, inasmuch as all hydrated salts are unsuited, for the following reason. If a hydrated salt be added to a solvent solution of a definite strength, the quantity of water present is increased by the amount present in the quantity of the hydrated salt that is dissolved. What part this water plays is still a moot point. Does it remain attached to the salt, or does it become part of the solvent? Until this question is settled, experiments with such salts only complicate a problem already sufficiently difficult. Nor can this complication be avoided by dehydrating the salt before adding it to the solvent solution; no water is indeed added to the solution, but the other objection mentioned above still remains; and we are met with a still greater difficulty in addition—the excess of dehydrated salt that is perforce added removes an unknown quantity of water from the solution, and the composition of the solvent solution is altered. Such an alteration is not of course fatal, but necessitates separate determinations of the amount of the salts present, involving an amount of labour which it would be foolish to undertake until it is seen from experiments with anhydrous salts that the method of investigation is likely to yield valuable results.

The salts examined were the chlorides of potassium and sodium and the nitrates of the same two metals. These salts present special advantages for this and all other solution experiments. They can be easily obtained pure. They crystallize from solution in the anhydrous state, and are not known to form hydrates except at low temperatures. The physical properties of their solutions have been more fully studied than those of any other salts. Their solubility presents no abnormalities on rise of temperature. They differ greatly in amount of their solubility at the ordinary temperature, and still more markedly in the effect of temperature on the amount dissolved. Above all, they are all sufficiently soluble in water at 20° C. to render any small experimental error of little consequence.

These four salts were arranged, for the purposes of experiment, in two series of four pairs, the two series being complimentary the one to the other.

(1) KCl in NaCl.	(2) NaCl in KCl.
(3) KCl in KNO_3.	(4) KNO_3 in KCl.
(5) $NaNO_3$ in NaCl.	(6) NaCl in $NaNO_3$.
(7) $NaNO_3$ in KNO_3.	(8) KNO_3 in $NaNO_3$.

The solubility of each of these salts in water at 20° C. was first determined, with the results given in Table I.

TABLE I.

Solubility of Single Salts at 20° C.

Salt.	I.	II.	Mean.	Molecules.
NaCl	35·92	35·89	35·905	11·048
KCl	34·49	34·55	34·52	8·329
$NaNO_3$	87·64	87·66	87·65	18·562
KNO_3.....	31·11	31·11	31·11	5·539

In parts per 100 of water and molecules per 100 H_2O.

In Table II. these results are compared with those given by other experimenters, and the mean of all my previous experiments published and unpublished.

TABLE II.

	NaCl.	KCl.	$NaNO_3$.	KNO_3.
Present mean ...	35·905	34·52	87·65	31·11
Former „ ...	35·69	34·72	87·61	30·72
Mulder	36·00	34·70	87·50	31·20
Gay-Lussac	36·10	34·68	88	
Kopp	.....	.....	88·70	31·96
Poggiale.....	36·01	.....	89·55	

In view of the close concordance of my present determinations and the long time allowed for saturation, along with the fairly close agreement with those of Mulder and Gay-Lussac, I feel justified in adopting my present mean as the true statement of the solubility of these four salts.

The solubility of the salts in pairs was then determined, with the precaution of adding excess of salt A to one and excess of salt B to the other of the duplicate experiments. The results are given in Table III., along with those previously obtained by me and those of Rüdorff.

Table III.

Salts.	Present determination.	Former result.	Rudorff.	
KCl and NaCl	44·70	45·60	45·6	18°·8
KCl and KNO_3.....	51·87	52·67	54·30	
NaCl and $NaNO_3$.....	78·89	76·93	79·89	
$NaNO_3$ and KNO_3 ...	134·21	135·29		

In parts of salt per 100 parts of water.

I shall have to return to this question later; so any discussion of the general accuracy of the above results will be best deferred till then. With regard to the composition of the total quantity of mixed salts in the saturated solution little need be said here. At first attempts were made to determine the ratio of the two metals in the case of the mixed chlorides and mixed nitrates by estimating the total chlorine and conversion into sulphate respectively; but the atomic weights of the two metals sodium and potassium differ by so small an amount, that all such indirect methods of analysis yield, of necessity, but approximate results on which no great reliance can be placed. In the case of the other pairs of salts the determination of the chlorine gives a direct method by which the ratios of the two salts can be ascertained, and one which can be trusted; but there is a still better method applicable to all four pairs of salts, which will be described further on.

The remainder of the research was conducted as follows:—

Solutions of the second salt in each of the eight pairs given on page 376 were prepared by weighing definite amounts of water (about 50 cub. cent.) to the nearest half milligramme, and adding to these the requisite quantity of the salt to form a solution of a definite molecular composition (n molecules of salt to 100 molecules of water). The salts used were carefully purified, the potassium and sodium chlorides by precipitation with hydrochloric-acid gas from solutions of the commercially pure salt, which had been previously treated with ferric chloride, followed by precipitation of the iron and other heavy metals that might be present by the pure carbonate of the metal. The salt thus precipitated with hydrochloric acid was thoroughly drained, washed repeatedly with pure hydrochloric acid, and finally dried by heating to 200° C. for several days. In some cases the salt was fused in a platinum dish at the lowest possible temperature, and in no case did the salt possess the slightest acid reaction. The

nitrates were purified in various ways ; the commercially pure salt was precipitated by alcohol, or by pure nitric acid ; in other cases subjected to repeated crystallization, and dried as above or fused. Too much care cannot be taken to ensure the use of pure salts in all saturation experiments ; for while a trace of impurity may not make its presence felt in other solution experiments, it is sure to vitiate the results of saturation, inasmuch as in these cases there is always present a considerable amount of undissolved salt ; and out of this the whole of the impurity is dissolved, thus raising unduly the percentage of salt dissolved. In this is to be found the explanation of the serious differences so often to be observed in all saturation experiments.

The salt solutions (solvent solutions) having been thus prepared, they were in several instances analysed by evaporation, in order to ascertain whether the method of preparation was sufficiently accurate for the purpose in view. The results are given in Table IV.

TABLE IV.

Salt.	Calculated.	Found.	Difference.
2 NaCl	6·5	6·5172	+0·0172
4 NaCl	13·0	13·0162	+0·0162
6 NaCl	19·5	19·520	+0·020
1 KNO_3	5·618	5·623	+0·005
3 KNO_3	16·854	10·860	+0·006

These determinations showed that this direct method of preparing the solutions was all that could be desired, as an error of 0·02, or one in 5000, is much less than that met with in even the most careful saturation experiments.

The solvent solutions were then saturated with the other salts, and the results with the eight pairs of salts are given in the following Tables V.–VIII. The Tables are arranged in the order already given, and each consist of two parts corresponding to the two series. The arrangement in each table is the same. In the first column is given the number of molecules of the second salt per 100 molecules of water, in the second the amount of salt per 100 parts of water that the above corresponds to ; in the third column the salt actually found (M.S. mixed salt) per 100 of water ; in the fourth the mean of the experimental results ; and in the fifth the difference between the fourth and second columns, that is, the amount

TABLE V.

KCl in Solutions of NaCl.

Mols. NaCl.	NaCl.	M.S.	Mean M.S.	KCl.	Mols. KCl.
0	0	34·49			
		34·55	34·52	34·52	8·329
2	6·5	35·849			
		35·897	35·873	29·373	7·087
4	13·0	37·657			
		37·755	37·706	24·706	5·961
6	19·5	39·966			
		39·865	39·916	20·416	4·926

NaCl in Solutions of KCl.

Mols. KCl.	KCl.	M.S.	Mean M.S.	NaCl.	Mols. NaCl.
0	0	35·92			
		35·89	35·905	35·905	11·048
1	4·144	38·554			
		38·508	38·531	34·387	10·581
2	8·289	40·953			
		41·053	41·003	32·714	10·066
3	12·422	43·714			
		43·729	43·722	31·300	9·631

TABLE VI.

KCl in Solutions of KNO_3.

Mols. KNO_3.	KNO_3.	M.S.	Mean M.S.	KCl.	Mols. KCl.
0	0	34·49			
		34·55	34·52	34·52	8·329
1	5·618	39·802			
		39·864	39·833	34·215	8·256
3	16·854	50·309			
		50·276	50·293	33·439	8·068

KNO_3 in Solutions of KCl.

Mols. KCl.	KCl.	M.S.	Mean M.S.	KNO_3.	Mols. KNO_3.
0	0	31·11			
		31·11	31·11	31·11	5·539
2	8·289	33·961			
		33·975	33·968	25·679	4·572
4	16·579	38·733			
		38·772	38·753	22·174	3·948
6	24·867	45·096			
		45·046	45·071	20·204	3·597
7·5	31·084	50·145			
		50·164	50·155	19·071	3·395

TABLE VII.

$NaNO_3$ in Solutions of NaCl.					
Mols. NaCl.	NaCl.	M.S.	Mean M.S.	$NaNO_3$.	Mols. $NaNO_3$.
0	0	87·64			
		87·66	87·65	87·65	18·562
2	6·5	83·843			
		83·844	83·844	77·344	16·379
4	13·0	81·503			
		.....	81·503	68·503	14·507
6	19·5	79·962			
		80·026	79·994	60·494	12·811

NaCl in Solutions of $NaNO_3$.					
Mols. $NaNO_3$.	$NaNO_3$.	M.S.	Mean M.S.	NaCl.	Mols. NaCl.
0	0	35·92			
		35·89	35·91	35·91	11·048
3	14·167	46·978			
		46·988	46·983	32·816	10·097
6	28·334	58·164			
		58·072	58·118	29·784	9·164
9	42·501	69·410			
		69·405	69·408	26·907	8·279

TABLE VIII.

$NaNO_3$ in Solutions of KNO_3.					
Mols. KNO_3.	KNO_3.	M.S.	Mean M.S.	$NaNO_3$.	Mols. $NaNO_3$.
0	0	87·64			
		87·66	87·65	87·65	18·562
1	5·618	94·186			
		94·266	94·226	88·608	18·764
3	16·854	107·474			
		107·821	107·648	90·794	19·227
5	28·09	121·085			
		120·610	120·848	92·758	19·643

Table VIII. (*continued*).

KNO_3 in Solutions of $NaNO_3$.

Mols. $NaNO_3$.	$NaNO_3$.	M.S.	Mean M.S.	KNO_3.	Mols. KNO_3.
0	0	31·11			
		31·11	31·11	31·11	5·539
1	4·722	35·064			
		35·096	35·080	30·358	5·405
2	9·444	39·560			
		39·445	39·502	30·058	5·352
3	14·167	44·114			
		44·229	44·172	30·005	5·342
6	28·334	59·614			
		59·541	59·578	31·244	5·563
9	42·501	75·399			
		75·063	75·231	32·730	5·827
12	56·668	91·092			
		91·225	91·159	34·491	6·141
15	70·835	107·050			
		107·590	107·320	36·485	6·496
18	85·002	123·424			
		123·410	123·417	38·415	6·840

dissolved of the first salt. The last column gives the molecules of the first salt present per 100 molecules of water. The molecular weights used throughout are :—

$NaCl = 58·5$, $KCl = 74·6$, $NaNO_3 = 85$, $KNO_3 = 101·1$.

With regard to the accuracy of these determinations one or two words only need be said. In the 27 duplicate experiments the sum of the differences between each pair amounts to 3·057 parts of salt in the 100 parts of water, giving a mean error of 0·113 ; but of the whole 27 only four much exceed this mean error, leaving 23 experiments with a total error of 1·359, and a mean error of 0·059, or $\pm 0·03$ from the mean. And it must not be forgotten that the results are parts per 100 of water and not percentages, and the error thus appears twice as great as it would have been had the other mode of calculation been employed.

The next point to be considered is the ratio of the two salts in the saturated solutions formed when water is treated with excess of both salts. This problem may now be attacked from two sides.

(1) That of direct experiment, and better even, since that is beset with difficulties, (2) that of indirect experiment, for it is evident that if the data derived from any pair of salts in the duplicate experiments be plotted the curves thus obtained will, if prolonged, intersect at the saturation-point of the salts when each is present in excess. The saturation-point thus obtained indirectly will depend not on one or two experiments

but on all the duplicate experiments in each series, and will, if it agrees with that obtained directly, be proof not only of the correctness of the latter, but also of the accuracy of the data from which it was itself derived. To plot* the results, however, on such a scale as to give the second place of decimals, is not so convenient as to find formulæ that will approximately represent the experimental results. The following satisfy this condition. M.S.=Total salt dissolved.

(1) KCl in Solutions of NaCl.

M.S. $=34{\cdot}52+n\ 0{\cdot}05707+n^2\ 0{\cdot}0545.$

Or, KCl $=34{\cdot}52-n\ 2{\cdot}6793+n^2\ 0{\cdot}0545.$

(2) NaCl in Solutions of KCl.

M.S. $=35{\cdot}91+n\ 2{\cdot}603.$

Or, NaCl $=35{\cdot}91-n\ 1{\cdot}541.$

(3) KCl in Solutions of KNO_3.

M.S. $=34{\cdot}52+n\ 5{\cdot}26.$

Or, KCl $=34{\cdot}52-n\ 0{\cdot}358.$

(4) KNO_3 in Solutions of KCl.

M.S. $=31{\cdot}11+n\ 0{\cdot}959+n^2\ 0{\cdot}261-n^3\ 0{\cdot}0065.$

Or, KNO_3 $=31{\cdot}11-n\ 3{\cdot}185+n^2\ 0{\cdot}261-n^3\ 0{\cdot}0065.$

(5) $NaNO_3$ in Solutions of NaCl.

M.S. $=87{\cdot}64-n\ 2{\cdot}378+n^2\ 0{\cdot}263-n^3\ 0{\cdot}01325.$

Or, $NaNO_3$ $=87{\cdot}64-n\ 5{\cdot}628+n^2\ 0{\cdot}263-n^3\ 0{\cdot}01325.$

(6) NaCl in Solutions of $NaNO_3$.

M.S. $=35{\cdot}91+n\ 3{\cdot}722.$

Or NaCl $=35{\cdot}91-n\ 1{\cdot}0.$

(7) $NaNO_3$ in Solutions of KNO_3.

M.S. $=87{\cdot}64+n\ 6{\cdot}65.$

Or, $NaNO_3$ $=87{\cdot}64+n\ 1{\cdot}03.$

(8) KNO_3 in Solutions of $NaNO_3$.

†M.S. $=31{\cdot}11+n\ 4{\cdot}429+n^2\ 0{\cdot}0663-n^3\ 0{\cdot}00153.$

Or, KNO_3 $=31{\cdot}11-n\ 0{\cdot}293+n^2\ 0{\cdot}0663-n^3\ 0{\cdot}00153.$

With the aid of these formulæ I have constructed the following Tables, representing the effect of each molecule of salt present in the solvent solution on the solubility of the other salt.

* Figs. 2–4, Plate VIII., give the general form of the curves on a small scale.

† Above 9 molecules per 100 H_2O.

KCl in sol. of NaCl.

Mols. NaCl.	M.S.	KCl.
0	34·52	34·52
1	35·15	31·90
2	35·88	29·38
3	36·72	26·97
4	37·65	24·65
5	38·73	22·48
6	39·91	20·41
7	41·18	18·43
8	42·58	16·58
9	44·07	14·82
10	45·68	13·18

NaCl in sol. of KCl.

Mols. KCl.	M.S.	NaCl.
0	35·91	35·91
1	38·51	34·37
2	41·12	32·83
3	43·71	31·28
4	46·32	29·74

KCl in sol. of KNO_3.

Mols. KNO_3.	M.S.	KCl.
0	34·52	34·52
1	39·78	34·16
2	45·04	33·80
3	50·30	33·45
4	55·56	33·09

KNO_3 in sol. of KCl.

Mols. KCl.	M.S.	KNO_3.
0	31·11	31·11
1	32·32	28·18
2	34·02	25·73
3	36·26	23·83
4	39·71	22·13
5	41·62	20·90
6	44·85	19·99
7	48·39	19·28
7·5	50·24	19·16
8	52·07	18·92

$NaNO_3$ in sol. of NaCl.

Mols. NaCl.	M.S.	$NaNO_3$.
0	87·64	87·64
1	85·39	82·14
2	83·78	77·28
3	82·52	72·77
4	81·49	68·49
5	80·67	64·42
6	79·98	60·48
7	79·34	56·59
8	78·67	52·67

NaCl in sol. of $NaNO_3$.

Mols. $NaNO_3$.	M.S.	NaCl.
0	35·91	35·91
1	39·63	34·91
2	43·35	33·91
3	47·08	32·91
4	50·80	31·91
5	54·52	30·91
6	58·24	29·91
7	61·96	28·91
8	65·69	27·91
9	69·41	26·91
10	73·13	25·91
11	76·85	24·91
12	80·57	23·91

$NaNO_3$ in sol. of KNO_3.

Mols. KNO_3.	M.S.	$NaNO_3$.
0	87·64	87·64
1	94·29	88·67
2	100·94	89·70
3	107·59	90·74
4	114·24	91·77
5	120·89	92·80
6	127·54	93·83
7	134·19	94·86
8	140·84	95·89

KNO_3 in sol. of $NaNO_3$.

Mols. $NaNO_3$.	M.S.	KNO_3.
9	75·22	32·72
12	91·18	34·52
15	107·31	36·47
18	123·42	38·42
20	134·01	39·57
21	139·23	

1. *Solutions containing* KCl *and* NaCl.

The saturated solution, when both salts are added in excess to water, was found to contain 44·70 parts of mixed salts to 100 parts of water. If this be the true solubility of the salts, and the formulæ given on p. 383 be correct, then

$$44{\cdot}70 = 34{\cdot}52 + n\,0{\cdot}5707 + n^2\,0{\cdot}0545$$

and

$$44{\cdot}70 = 35{\cdot}91 + n\,2{\cdot}603,$$

the former equation giving the molecules of NaCl, the latter those of KCl present in the saturated solution.

The equations worked out give

9·394 molecules NaCl per 100 H_2O

and

3·777 molecules KCl per 100 H_2O,

or

30·54 parts of NaCl per 100 of water

and

13·99 parts of KCl per 100 of water,

or

44·53 parts of mixed salts per 100 of water ;

an error of −0·17 part per 100 of water, showing the correctness of both the formulæ and the direct determination.

From the above calculation we find that the 44·7 parts of mixed salts contain 14·075 parts of KCl and 30·625 parts of NaCl; or, in molecules per 100 H_2O, 3·396 KCl and 9·423 NaCl ; or, 1 part of KCl to 2·176 parts of NaCl and 1 molecule KCl to 2·775 molecules NaCl.

2. *Solutions containing* KCl *and* KNO_3.

The saturated solution formed when both salts are added in excess to water was found to contain 51·87 parts of mixed salts to 100 parts of water. If this be the true solubility, and the formulæ be correct, then

$$51{\cdot}87 = 34{\cdot}52 + n\,5{\cdot}26,$$

$$51{\cdot}87 = 31{\cdot}11 + n\,0{\cdot}959 + n^2\,0{\cdot}261 - n^3\,0{\cdot}0065 ;$$

the former equation giving the molecules of KNO_3, the latter those of KCl present in the saturated solution.

The equations worked out give

3·298 molecules KNO_3 per 100 H_2O

and

7·925 molecules KCl per 100 H_2O,

or

18·95 parts of KNO_3 per 100 of water

and

32·84 parts of KCl per 100 of water ;

an error of $-0{\cdot}08$ part per 100 of water. The formulæ and the direct determination are therefore correct.

3. *Solutions containing* NaCl *and* $NaNO_3$.

The saturated solution formed when both salts were added in excess to water was found to contain 78·89 parts of mixed salts to 100 parts of water. If this be the true solubility, and the formulæ be correct, then

$$78{\cdot}89 = 87{\cdot}64 - n\,2{\cdot}378 + n^2\,0{\cdot}263 - n^3\,0{\cdot}01325,$$
$$78{\cdot}89 = 35{\cdot}91 + n\,3{\cdot}722.$$

The former equation gives the molecules of NaCl, the latter those of $NaNO_3$ present in the saturated solution.

The equations worked out give

7·662 molecules NaCl per 100 H_2O

and

11·55 molecules $NaNO_3$ per 100 H_2O,

or

24·91 parts of NaCl per 100 of water

and

54·55 parts of $NaNO_3$ per 100 of water ;

an error of $+0{\cdot}57$ part per 100 of water. The formulæ and the direct determination therefore very fairly agree.

4. *Solutions containing* $NaNO_3$ *and* KNO_3.

The saturated solution formed when both salts are added in excess to water was found to contain 134·21 parts of mixed salts to 100 parts of water. If this be the true solubility, then

$$134{\cdot}21 = 87{\cdot}64 + n\,6{\cdot}65,$$
$$134{\cdot}21 = 31{\cdot}11 + n\,4{\cdot}429 + n^2\,0{\cdot}0663 - n^3\,0{\cdot}00153.$$

The former equation gives the molecules of KNO_3, the latter those of $NaNO_3$ present in the saturated solution.

The equations worked out give

7·005 molecules KNO_3 per 100 H_2O

and

20·039 molecules $NaNO_3$ per 100 H_2O,

or

39·34 parts of KNO_3 per 100 of water

and

94·60 parts of $NaNO_3$ per 100 of water;

an error of $-0{\cdot}27$ part per 100 of water. The formulæ and the direct determination therefore agree.

The mutual solubility of potassium and sodium nitrates has been specially studied by Carnelley and Thomson, whose

results are given in a paper on the Solubility of Isomeric Organic Compounds &c., published in 1888 (Chem. Soc. Journ. Trans. 1888, pp. 782–802). Their results are by no means concordant, owing no doubt to the method of conducting the experiments, for which reference must be made to the original paper. The general form of the curves representing their results is the same as that given by my experiments, as will be seen by reference to fig. 4, Plate VIII., in which I have plotted my results, and side by side with them the curves given by Carnelley (*loc. cit.*).

Here the subject must be left for the present. For although there are many points of interest raised, and some general conclusions of importance to be deduced, the discussion of these is best deferred until experiments at present in progress on the molecular volumes of such solutions have been completed.

XLV. *On the Maximum Density of Water.*

By H. M. Vernon, *Scholar of Merton College, Oxford* *.

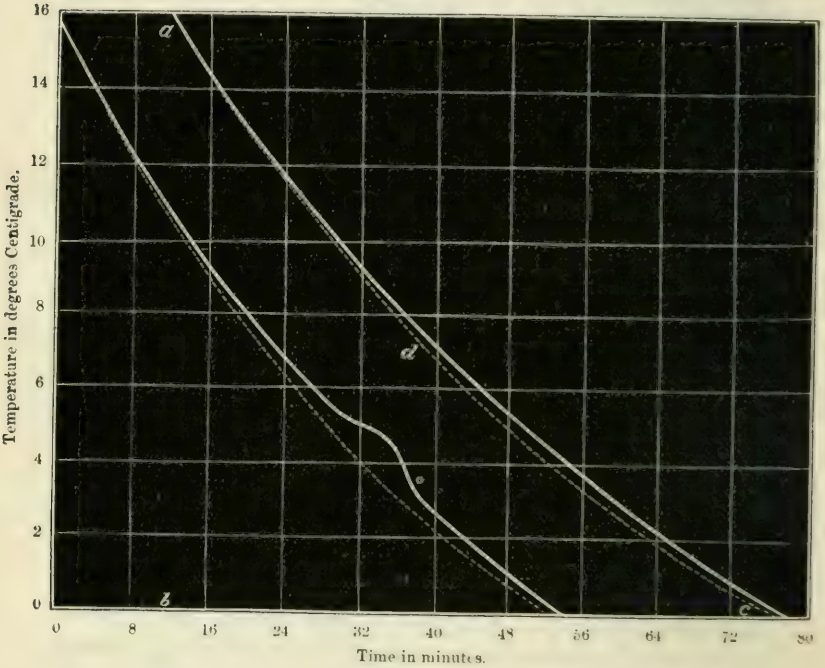
THOUGH the fact that water has not a regular dilatation, but reaches a maximum density at about 4° C., has been universally known for a very long time, apparently no explanation has yet been offered of this seeming anomaly, which is of such vast importance in nature. The object of this paper is to bring forward a few experiments which afford an interpretation of the fact.

If the fact of the irregular dilatation of water be carefully considered, it will be seen that the only possible explanation of it is that some change in the position of the water molecules towards each other takes place at about 4° C., whereby such a considerable variation in the density is caused. It is, therefore, probable that at this temperature some thermal change will also take place. If a volume of water be heated and allowed to cool without being subjected to any external variations of temperature, it is evident that if such a thermal change does occur at 4° C., the rate of cooling of the water will not be regular at this point. To test this, experiments were made on the rate of cooling of water from about 30° C. to slightly below 0° C.

A volume of distilled water, varying in different experiments from 30 cub. centim. to 60 cub. centim., was placed in a glass flask which was suspended inside a large beaker surrounded by a freezing-mixture of ice and salt. The vessel

* Communicated by the Author.

containing the freezing-mixture and the beaker itself were well covered up, and the temperature was found to remain constant throughout the experiment. The thermometer used was a standard one, graduated in tenths of a degree; and as all readings were taken with a cathetometer, it was read to the hundredth of a degree. The water was then warmed to about 30° C., and readings taken of the thermometer at intervals of a minute, till it had cooled to about −3° C., when ice began to form. In the figure will be seen the curve for the



rate of cooling which was thus obtained. The curve is only given up to 16° C., as above this it is quite regular. From about 14° C. the cooling begins to take place slightly less rapidly than would be the case if no internal thermal change were taking place, and continues getting less and less rapid till from about 5°·5 C. to 4°·7 C. it almost stops. At 4·7° C. it suddenly begins to sink rapidly again till about 3° C. After this point the curve becomes regular again. The part of the curve from 30° C., if produced on the supposition that the curve is regular, gives the dotted-line curve in the figure.

Water has been found to have its maximum density at

4°·07 C. by Rosetti, at 4°·1 C. by Hällstrom, at 4°·08 C. by Kopp, and at 4°·0 by Despretz; but here the maximum point of the irregularity in the curve is at 4°·7 C. There can be no doubt that such is the case, as several separate cooling determinations gave this temperature as the maximum, it being also corrected for the thermometer, which gave the freezing-point of water as +·08° C. Also the rate of cooling of oil was taken by the thermometer, and was found to be quite regular; so the difference could not have been due to a thermometric error.

In these experiments the water was not stirred; and it is to this fact that the great irregularity in the curve at 4°·7 C. is due. The cooling effect produced in the outer layers of water in the flask mainly reach the inner layers of water and the thermometer-bulb by convection-currents set up by the change in the density of the water with change of temperature. The inside layers will therefore always have a slightly higher temperature than the outside layers. When the temperature of the outside layers has cooled to near 4° C., when the density no longer increases with fall of temperature, the convection-currents will be stopped, and at a slightly lower temperature, when the density decreases, will begin to be set up in an opposite direction. This explains why there is a sudden pause in the curve for the rate of cooling, and also why directly after this the temperature sinks rapidly for a degree or two and then sinks much less rapidly; for this is due to the cold layers, which had been accumulating while the cooling almost stopped, being suddenly brought into contact with the thermometer-bulb. This experiment, therefore, merely serves to show the change in the density of water at about 4° C., and that the cooling effect reaches from the outside to the inside of the flask mainly through convection-currents, and not by radiation or conduction.

Experiments were then made on the cooling of water when stirred. A beaker containing 100 cub. cent. distilled water was suspended in another large beaker surrounded by a freezing-mixture. The smaller beaker was closed by a tightly-fitting bung, through which passed the thermometer and a light glass-rod stirrer. This was moved up and down regularly at intervals of about four seconds, during the whole period of cooling, by means of a cord passing over two pulleys. The second curve in the figure represents the rate of cooling. The curve above 14° is quite regular; and this curve, produced on the supposition that the curve is regular, gives the dotted-line curve in the figure. It will be seen that there is no sudden change in the curve at any point, but that the irregularity

seems to be greatest at about 4° C., though it is only very slightly marked.

The space between the two curves is a measure of the heat evolved in the cooling of the water. By calculating its area, and also the area of the figure *a b c d*, it was found that the specific heat of water is increased, on an average, from 12° C. to 0° C. by about 3 per cent. Only a very rough estimate can be arrived at in this way, as it is not possible to calculate the position of the dotted-line curve with any exactness. It is enough, however, to show that there is a material increase in the specific heat of water at temperatures near to that of its maximum density.

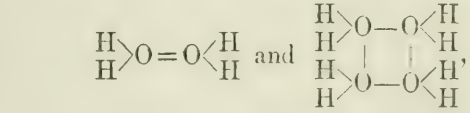
We have now to see to what extent the results obtained by cooling correspond with the variations in the dilatation of water. The density determinations of Rosetti (*Ann. Chim. Phys.* (4) x. p. 47), plotted out as a curve, show that down to about 16° C. the density increases regularly with decrease of temperature. From this point downwards the rate of increase of density begins to gradually get smaller, it getting less and less till at 4°·07 C. it stops. From this point the density begins to gradually decrease. If the dilatation were regular, the density of water at 4° C. would be much greater than is actually the case; that is, the density of water in the state of molecular aggregation it exists in at 4° C. is considerably less than it would be if the dilatation were regular, and no molecular change took place. This fact serves to explain why water below 4° C. begins to decrease in density.

The change in the density of water, which, as has been shown, is attended by an evolution of heat, can only be due to water molecules aggregating together, and forming more complex molecules than before existed. As, therefore, from 14° C. downwards the aggregated molecules are being formed in larger and larger quantities, whilst fewer and fewer of the unaggregated molecules are left, the lesser density of the aggregated molecules at last at 4° C. counteracts the greater density of the unaggregated molecules; and from this temperature downwards, when fewer still of the unaggregated molecules remain, the density of the water begins to decrease instead of increase. We do not know at what temperature the maximum number of aggregated molecules is formed; but the curve for cooling appears to have a slight maximum at about 4° C. So it may be taken that the density of water begins to decrease when about half of the molecules present have undergone aggregation. It is not necessary, however, that the maximum of the irregularity in

the curve for cooling should correspond with the temperature of maximum density of water.

We see then that, allowing for the effect of temperature, ordinary molecules of water have the greatest density, aggregated molecules have a lesser density, and ice, which must contain molecules in a still greater state of aggregation, has the least density.

Raoult, from his experiments on the molecular lowering of freezing-points (*Ann. Chim. Phys.* (6) ii. p. 66), concluded that while solvents such as acetic acid and benzene had molecular weights expressed by their ordinarily received formulæ, water had a molecular weight four times as great; that is, its molecular formula was $(H_2O)_4$. From analogy with other liquids, as acetic acid and hydrofluoric acid, and from the fact that at ordinary temperatures water is liquid, while the similarly constituted hydrides of sulphur, selenium, and tellurium are gaseous, it is probable that when water-vapour condenses it undergoes molecular aggregation. Water molecules from 100° C. to about 4° C. will probably, therefore, have the formula $(H_2O)_2$; and below 4° C. these will condense to $(H_2O)_4$ molecules. In constitution these condensed molecules may be considered merely as molecular compounds, or, what is really more simple, as atomic compounds linked thus:—



with oxygen in the tetravalent state.

We must now examine whether the evolution of heat taking place when water is cooled to 4° C., that is to say, the increased specific heat of water at this temperature, shows itself in the determinations of observers on the latent heat of fusion of ice and the specific heat of water. Regnault has determined the specific heat of water from 0°–40° C., 0°–80° C., 0°–120° C., &c, but not for smaller temperature-intervals than these. If, however, these results are calculated out for 20° C., 60° C., 100° C., &c, and a curve plotted out, it will be found that the specific heat of water for the interval 0°–40° C. is appreciably greater than we should be led to suppose from the specific heats at higher temperatures.

A. W. Velten (*Annalen*, 1884, p. 61) has made two series of determinations of the specific heat of water. By the method of mixing, the specific heat was determined for different intervals from 4°·7 C. to 100° C. For the interval

4°·7–42°·9 C. the specific heat was found to be ·9943; for the interval 7°·38–41°·1 C. it was ·9863: again, for the interval 8°·24–93°·6 C. it was ·9873, and for the interval 11°·78–93°·0 C. it was ·9837. Several other determinations showed that for temperatures near to 4° C. the specific heat was greater than the normal. By means of the ice-calorimeter the specific heat was determined for various intervals from 0° C. to 100° C. These results show that the specific heat is about 2 per cent. greater from 0°–7°·31 C. than from 7°·31–10°·81 C., and at higher temperatures. There seemed also to be another slight increase in the specific heat at about 18° C.; but the mixing experiments, in which it is possible to attain greater accuracy, do not show this, so it is probably not the case. If it were so, the curves for the cooling of water would also show an irregularity; they were, however, quite regular at this point.

As the latent heat of fusion of ice is determined by mixing it with water of known temperature, an appreciable difference should be observed in the values obtained, according as the temperature of the mixture is near 4° C. or considerably removed from it. In both Regnault's experiments and those of Provostaye and Desains (*Ann. Chim. Phys.* 1843. pp. 18 and 27), the temperature of the mixture varied from 7°·2 C. to 18° C.; but no regular variations in the values for the latent heat appear. The values vary among themselves from 78·74 to 79·26 units in Regnault's experiments, and from 78·75 to 79·46 in those of Provostaye and Desains; so the variation might be masked by experimental error. In Person's determinations the temperature of the mixture was about 4°·8 C., and the value 80 was obtained. This seems to show that the specific heat of water is increased at about 4° C., as though this heat is evolved in all the determinations; yet in those in which the mixture had a higher temperature, this heat was spread over a greater interval, and so would not produce so appreciably great an effect.

We see, then, that both the specific heat and the heat of fusion of ice determinations confirm the results obtained by cooling. There can be, therefore, no doubt as to the molecular change taking place at 4° C. The method of cooling affords a simple and accurate means for confirming any supposed irregularities in the specific heat of a liquid; and, as the above results show, in the density of a liquid as well, provided it is not stirred during the cooling.

The University Laboratory, Oxford.

XLVI. *On some Effects of small Quantities of Foreign Matter on Crystallization.* *By* Charles Tomlinson, *F.R.S., F.C.S.**

I WAS interested in reading an account of a lecture by Professor Judd, delivered at the Royal Institution on January 30 last, on some phenomena of crystallization. I was present at the same Institution on one of the Friday evenings upwards of forty years ago, when Professor Faraday performed an experiment which greatly impressed me. He poured water into a test-tube, and added to it an intense colouring-matter, such as sulphate of indigo, and then placed the tube in a freezing-mixture: the water in freezing drove the whole of the colouring-matter into the axis of the tube, so that it could be poured away, and, the cavity being rinsed out, a plug of pure transparent ice, entirely free from colouring-matter, was withdrawn. A similar experiment was tried with the addition of sulphuric acid to the water, and in a third experiment of ammonia; and in these cases also, the water in freezing expelled both the acid and the alkali, so that the ice in each case on being melted could be tested for either with negative results. In order to free the resulting ice from air particles, the contents of the tube were gently stirred with a feather, and reference was made to the rapidity with which melting ice reabsorbs air, a useful provision in the case of aquatic plants and animals, as was recently pointed out, when referring to the necessity of breaking the ice in fish-ponds.

A few years later, it was noticed that a large block of Wenham Lake ice, when illuminated by the electric light, presented a banded structure, which Faraday explained with reference to the experiments above noticed. Suppose the first layer of water in a still lake to freeze, it would reject any saline or other foreign matter into the layer of water below, and should the temperature continue to fall, the second layer would be unable to reject the particles derived from the first in addition to its own, and so this double set of particles becoming entangled in the ice, would so far alter its structure that it may be called *amorphous*, while the first layer would be *crystalline*. As the freezing proceeded, the third layer would be in an analogous position to the first, and the fourth layer would be in a similar condition to the second. In this way we might have alternate bands of crystalline and amorphous ice to a considerable depth.

Among the Finchley gravels we may sometimes pick up

* Communicated by the Author.

pebbles known as *banded* quartz. At one time I had several hundred specimens, most of which I have distributed among geological acquaintances. They consist of alternate bands of crystalline and amorphous quartz, and the latter variety being more porous and softer than the former, became abraded during the rolling on the ancient sea-beach, so that the harder crystalline portions project like the teeth of a saw. Now there must have been a time in the history of this planet when quartz was in a state of fusion, and it would probably contain minute particles of matter entangled within it. Supposing the temperature to have become sufficiently reduced for crystallization to set in, the first layer in crystallizing would reject its foreign matter into the second layer, and thus form two layers of crystalline and amorphous quartz; the process being repeated, we might have ten or a dozen alternate bands thus formed, the breaking-up of the mass into smaller fragments and their rolling into pebbles under the tidal action being subsequent events.

Such a suggestion is of course inadequate to account for the formation of siliceous minerals. Indeed, in the present state of our knowledge, it is quite impossible to do so, and the trivial names of the different varieties sufficiently point to our ignorance. In the formation of the agates it is evident that the successive layers were gradually formed at different times, and the name of this mineral is said to be derived from the river where specimens of it were found, namely, the *Achates* in Sicily, now known as the Drillo, in the Val di Noto. It is true that the carnelian is named from its resemblance to *caro, carnis*, "flesh," as applied to the red variety, but this name is not appropriate to the yellow. Onyx is so called from its resemblance to the human *nail*, ὄνυξ, *unguis*; but sardonyx is derived, according to some, from *Sardes* in Lydia, or from *Sardo*, the Greek name for Sardinia, as chalcedony is from *Chalcedon* in Bithynia. One of the most curious derivations is a variety of chalcedony of an apple-green colour, due to oxide of nickel, known as chrysoprase, from χρύσεος, "beautiful," and πράσον, "a leek." Other siliceous minerals with trivial names might also be referred to.

Professor Graham read a paper before the Royal Society in 1864 on the properties of Silicic Acid and other analogous colloidal substances, in which he says:—"The formation of quartz crystals at a low temperature, of so frequent occurrence in nature, remains still a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from solutions of silicic acid which are extremely dilute. Dilution, no doubt, weakens the colloidal character of such

substances, and may therefore allow their crystallizing tendency to gain ground and develope itself, particularly where the crystal once formed is completely insoluble, as with quartz." Prof. Graham found that a liquid silicic acid of 10 or 12 per cent. coagulates or pectizes spontaneously in three hours at the ordinary temperature, and immediately when heated. A liquid of 5 per cent. may be preserved for five or six days; a liquid of 2 per cent. for two or three months; and a liquid of 1 per cent. had not pectized after two years. Dilute solutions of 0·1 per cent. or less are probably unalterable by time, and hence the possibility of soluble silicic acid existing in nature. It was not found that any solution, weak or strong, of silicic acid in water showed any disposition to deposit crystals; but it always appeared on drying as a colloidal glassy hyalite.

In connexion with this subject, we may refer to Professor Bischoff in his Chemical and Physical Geology (Cavendish Society). He states that crystals of gypsum, thirteen lines in diameter, have been formed within four or six years on the thorn walls of salt-works, from drops of brine containing sulphate of lime. Gypsum dissolves in 460 parts of water; the water of some springs contains 1-10,000th of silica, so that this solution is about twenty-two times more dilute than the former. Supposing a crystal of quartz, one inch in diameter, to form under circumstances similar to those that produce a gypsum crystal of the same dimensions, rather more than a century would be required; the water percolating through the thorn faggots, and depositing nothing but silica, would in that time form a crystal of quartz consisting of 4,766,652 concentric layers of silica, each about one millionth of a line in thickness; but as the water of springs usually contains much less than 1-10,000th of silica, the time would probably have to be doubled, or even further increased; but such periods are by no means remarkable in geological phenomena.

In the early proceedings of the Geological Society, Mr. Bowerbank described some moss agates from Oberstein, containing remains of sponges. In 1848 Mr. Hamilton stated that the real agates of Oberstein are found in igneous rocks, so that they could not contain the remains of organic bodies. Whereupon Mr. Bowerbank produced sections of moss-agates, and placed them under a powerful microscope, when Mr. Hamilton admitted that they certainly did contain remains of spongeous structure*, but how far they are really found at

* The chalk flints best known to me are those found near Salisbury, and they commonly have a spongeous nucleus.

Oberstein, or merely brought there to be cut and polished, is another question. It subsequently became known that large numbers of these agates were imported from Brazil and other places.

The effect of small portions of foreign matter in modifying the structure and physical properties of siliceous minerals is a difficult subject, and often one of no little embarrassment to the mineralogist. In agate, for example, there may be 98 per cent. of silica, and minute portions of iron, in zigzag lines, as in the variety known as *fortification* agate; in other specimens, in various forms of animals and plants. These lines seem to be the edges of successive layers of material during the process of formation. Advantage has been taken of these lines to stimulate the artist to complete some of them into the forms of natural objects, forming what the French call *agates zoomorphytes*. These curiosities were in demand among the ancients. Thus Pliny (Lib. 37, Cap. 75, &c.) refers to three methods of manufacture, and describes an agate, the natural markings of which represent Apollo and the Nine Muses. In the British Museum there is a globular or Egyptian Jasper, which exhibits in the two fractured surfaces a likeness of the poet Chaucer. There is no reason to suppose that this has been doctored, but of course there is a strong temptation to fabricate these trifles, since they fetch a high price. Brard, in his *Minéralogie appliquée aux Arts*, describes how chalcedony may be etched with a metallic solution, such as blue vitriol in aquafortis, the result on drying being corroded lines of a brown colour. But he adds that designs produced in this way have a more finished appearance than the natural markings. Italy still continues to be the seat of this manufacture, as it probably was in Pliny's time.

Various devices are adopted at Oberstein for conferring an ornamental value on agates and other pebbles, whether native or imported. In one process the cut stone is covered with a layer of carbonate of soda, and heated to redness in a muffle. This produces a white opaque enamel, as hard as the stone itself, and adapted to cameo cutting. A similar result was produced during the great fire at the Tower of London some years ago, when many of the gun-flints encountered a rain of fused nitre, and so became encrusted with white enamel. Advantage is taken of the banded structure of some of the pebbles to colour the amorphous quartz artificially. The pebbles are washed and dried and then placed in an aqueous solution of honey or of sugar, about half a pound to a pint. The vessel is then put on a stove, or in hot ashes, and fresh liquid is supplied from time to time, so as to keep the stones

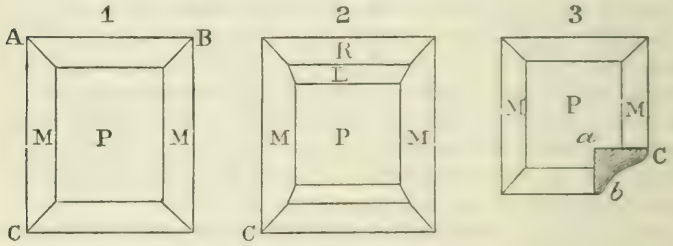
always covered. In this state they remain for two or three weeks, when they are transferred to a vessel containing commercial oil of vitriol, and gently heated. After some hours the stones are washed, dried on the stove, and transferred to the lapidary. After being cut they are steeped in oil for a day ; this causes small crevices to disappear, and gives a better lustre to the stones after polishing with oil and bran. The action of the sulphuric acid is to fill up the porous bands with carbon so as to produce greyish-brown or black stripes, while the non-absorbent bands become opaque white. Onyxes are prepared from Brazilian pebbles. A fine citron-yellow, uniform or in stripes, or in cloudy patches, is given to chalcedony by first drying the stones on a stove, and then immersing them for two or three weeks in hydrochloric acid. This contains a little iron, which is probably the source of the colour. A blue colour is produced by steeping the chalcedony in a solution of protosulphate of iron, and then in one of prussiate of potash. Other colours are similarly produced by forming precipitates within the stone. Even cochineal will impart its colour to agate. By the action of heat and various chemicals a great variety of ornamental pebbles are manufactured, some of which fetch a high price, such as the milky-white chalcedonies, with dendritic brown and black figures. Striped stones are converted into sardonyxes, and stones of one colour contract true carnelian tints. In some cases the pebbles are dried on a very hot stove during some weeks, then wetted with sulphuric acid, and raised to a red heat in a luted crucible ; they are then allowed to cool slowly, and the effect of the heat has been to deprive the hydrated oxide of iron of water, when the oxide combining with the silica develops the carnelian colour.

It would be a useful but difficult inquiry to determine the influence exerted by small quantities of apparently foreign or accidental impurities in modifying the structure of siliceous and other minerals. These presumably accidental ingredients bear the odd and apparently inappropriate name of *Mineralizers*. Their effect in producing a molecular change in structure seems to be undoubted, but the necessity for a searching inquiry seems to be evident, on account of the contradictory statements that are occasionally met with. For example, the green colour of the emerald is said to be due to chromium oxide, but Lewy* attributes it to the presence of a minute proportion of an organic hydrocarbon, which is dissipated by a strong heat, which would have no effect on chromium

* *Ann. de Chemie*, 1858, t. liii.

oxide. Badly coloured carnelians are converted by the action of heat into a uniform red.

The influence of small quantities of foreign matter, in modifying structure, may also be noticed in some cases of saline compounds. A striking experiment may be shown on a large scale with a supersaturated solution of potash alum. If a nucleus be added, octohedral crystals slowly descend, until the whole of the solution becomes solid. But if to the boiling solution a pinch of carbonate of potash be added, there is a brisk momentary effervescence on the surface, and when the solution is cold it will deposit, not octohedral, but cubic crystals of alum. So also sal-ammoniac crystals are modified by the presence of small doses of urea or of boracic acid. Common salt is another case, when under the influence of a small quantity of corrosive sublimate. Pasteur's discovery of two unsymmetrical varieties of tartaric acid* are also well known, but his curious experiments on bimalate of ammonia will bear repetition †. This salt crystalizes at ordinary temperatures in two forms: first, in that of a right rhombic prism in which the edges are bevelled; secondly, one in which the form is the same, but the top and bottom edges have a double bevel, as at R L, fig. 2. The



bevels are also striated, but the striæ are not found on the side truncations M, M. If one or more of the solid angles be rubbed or filed down, as at *a*, *b*, *c*, fig. 3, and placed in a pure solution of the salt, the damage becomes restored in a few hours. But if the solution be contaminated with some of the products of decomposition of the salt, occasioned by the heat, not only are the angles restored, but the upper and lower edges become bevelled, as in fig. 2. The presence of these secondary faces seems to be due to impurities in the solution, and to exert some action on the growth of the crystal in its

* *Ann. de. Chem. et de Phys.* sér. 3, xxiv. et xxvii.
† *Ibid.* xlix.

different dimensions; that is, a deposit takes place more rapidly in a perpendicular than in a lateral direction, the crystal increasing much more in length A C than in width A B in a solution which gives the bevellings; while in another solution in which the secondary faces are not produced, the crystal increases a little more in width than in length. A complete crystal which had not the secondary faces, was bisected in the direction of its cleavage plane; one portion was put into the solution which gives the bevellings, fig. 2, and the other into the pure solution, which produces only the single bevel, No. 1. The conditions in other respects were the same, the two vessels being of the same size and material, placed side by side on the same table and exposed for the same number of hours at the same temperature; and yet next morning the two crystals were completely restored, one with its double and the other with its single bevelled edges, as in figs. 1 and 2; but the crystal No. 1 was much wider than No. 2, and No. 2 much longer than No. 1.

It was supposed that if this mode of increase bore relation to the variation in form, the double bevelment might be excited in the pure solution which does not produce it under normal conditions, by means of some contrivance which would prevent the lateral growth of the crystal, while it encouraged the abnormal growth lengthwise. Accordingly, a single bevelled crystal, fig. 1, had slips of tin foil or metallic paper attached to its lateral facets, while its upper and lower bevels were rubbed down. The crystal thus prepared was put into a pure solution under conditions like those of the crystal in the impure solution. Next day it was found that the crystal had resumed its regular form, the bevels being produced as in No. 2. The experiment was varied in different ways, and measurements were made showing the rate of increase in length and in width of the two varieties of the salt. Hence it appears that foreign matters in solution may, in the act of crystallization, change the relations of increase according to the three dimensions of the salt, an effect which is as much physical as chemical. The relations of the mutual attraction of the saline molecules, according to their different sides, thus become changed by the presence of a minute quantity of foreign matter, and new relations are set up between the number of particles deposited in the unit of time; thereby allowing or disallowing the existence of certain facets compatible nevertheless with the primitive form of the crystal.

Highgate, N.,
March 31, 1891.

XLVII. *A Comparison of the Bourdon, the Tait, and the Amagat High-Pressure Gauges.* *By* C. Barus*.

1. *PRELIMINARY.*—In my earlier work † I was obliged to content myself with empiric pressure measurement. I found, by comparing different Tait gauges of my own with a large Bourdon gauge, that so long as pressure continually increased from zero, the relation between the indications of each under like conditions of pressure was linear; but that when pressure again decreased from a high value (1000 atmospheres or more), this relation changed to a markedly curvilinear locus, terminating, however, in the original zero ‡. I inferred that so long as increasing pressures alone were applied, both gauges could be used with safety. The present work, in which the two gauges are directly compared with Amagat's "manomètre à pistons libres," corroborated this inference, and shows that the bow-shaped cycles represent the actual motion of the free end of the Bourdon tube. From this point of view the data are important, for they supply an example of purely mechanical hysteresis, and possibly of metallic volume-lag. The data also show that cyclic change is absent in the Tait gauge, and indicate a way in which this instrument may be adapted for the precise measurement of pressures of any value whatever.

2. *Amagat's Manomètre.*—The instrument § in possession of the Physical Laboratory, U.S.G.S., is constructed for measuring pressures as high as 3000 atmospheres. At this limit the height of the compensating column of mercury (the diameters of the two pistons being ·549 centim. and 12·171 centim. respectively) will be about 464 centim. To read so long a column with reasonable facility, I fixed a painter's ladder in a vertical position, and permanently attached to one side of it both the manometer-tube, and a millimetre-scale which I ruled with care on a sufficiently long strip of brass. A round leather belt, passing from top to bottom of the ladder, and everywhere within easy reach, was suitably connected with the mechanism for rotating the two pistons. I was thus able to give the two pistons the rotational movement immediately before taking the gauge-reading, no matter what my position on the ladder might be.

I found by trial, that by using the thick mineral machine-

* Communicated by the Author.
† This Magazine, [5] xxx. p. 338 (1890).
‡ *Ibid.* plate x. The zero is not quite regained.
§ Marked "E. H. Amagat, Lyon, 1890."

oil mentioned in my last paper*, the manomètre could be at once connected with the screw-compressor. I also floated the lower piston in this oil. Thus the same oily liquid is used for the transmission of pressure, with advantage, I think, throughout the system of apparatus.

3. *The Bourdon Gauge.*—The gauge used was the same to which my earlier measurements apply, having a tube of steel or iron†. I made two series of comparison of this gauge with the manomètre. In the first of these, the usual multiplying gear was used; in the other the excursions of the free end of the Bourdon tube were read off directly with a Fraunhofer microscopic micrometer, after the multiplying gear had been removed. Tables I. and II. contain examples of the measurements made. There are four series of observations, two of them within an interval of 500 atmospheres, the other two within 1000 atmospheres. In both cases two values are shown for each stop of pressure. Table II. gives the micrometer position of the free end of the Bourdon tube prolonged, in centim. /40, this being the scale part of the micrometer. As usual, the observations were made in triplets, two at the manomètre, including each one at the Bourdon gauge.

TABLE I.—Cyclic Comparisons of the Bourdon Gauge (multiplying gear) with the Amagat Manomètre.

Bourdon.	Amagat.	Bourdon.	Amagat.	Bourdon.	Amagat.	Bourdon.	Amagat.
Atm.	Atm.	Atm.	Atm.	Atm.	Atm.	Atm.	Atm.
*188	*185	444	447	991	982	650	653
174	173	433	435	977	962	645	647
322	325	224	219	847	815	855	860
312	314	225	221	837	804	838	832
457	459	83	78	651	606	985	982
446	448	84	78	646	601	977	960
316	314	20	16	475	421	964	954
313	311			475	420	950	957
162	157			262	223	840	809
165	158	†21	†16	263	225	834	802
27	23	242	241	28	16	631	587
		231	232			626	582
		472	474			440	386
**29	**24	457	461	‡30	‡19	440	386
172	170	660	660	251	250	260	215
168	165	640	642	245	243	264	222
317	318	859	849	465	468	35	23
305	306	844	833	458	458		
462	464						

* First series. ** Second series. † Third series. ‡ Fourth series.

* This Magazine, [5] xxxi. p. 10 (1891).

† Probably of iron; unfortunately I cannot tell which without analysing the tube or breaking it.

TABLE II.—Cyclic comparisons of the Bourdon Gauge (Fraunhofer Micrometer) with the Amagat Manomètre.

Bourdon.	Amagat.	Bourdon.	Amagat.	Bourdon.	Amagat.	Bourdon.	Amagat.
cm./40.	atm.	cm./40.	atm.	cm./40.	atm.	cm./40.	atm.
*19·69	* 0	6·12	914	†18·92	† 1	6·33	901
16·04	228	7·94	753	15·83	242	8·20	756
16·12	227	8·36	753	15·87	239	8·39	739
11·93	523	11·20	535	11·91	523	11·08	539
12·19	518	11·28	534	12·20	513	11·08	539
8·40	772	15·18	251	8·86	730	14·80	270
8·58	765	15·18	254	9·18	720	14·80	274
5·23	969	18·97	0	5·25	969	19·06	0
5·66	956			5·70	956		
6·02	914			6·16	935		

* First series. † Second series.

4. It appears from Table I. that if allowance be made for errors of reading, the observations of the first two series lie on a straight line. The factors, Bourdon/Amagat, in the first series are ·998 in the on march and ·987 in the off march. In the second series these factors have changed to ·984 and ·992 respectively. It follows from both series that within 500 atmospheres a cyclic march does not appreciably occur.

In the third series, which shows a change of rate above 700 atmospheres, on, the return march is distinctly cyclic, and at 500 atmospheres the zone shows a breadth of almost 50 atmospheres. The zero is regained within 10 atmospheres. The mean factors are ·991 below and 1·008 above 700 atmospheres, on. The factor of the off march is of no interest. Remarks of the same kind apply in cases of the fourth series, where the factors are ·982 below and 1·072 above 700 atmospheres, on. Some irregularity in this series is due to unwarrantably vigorous tapping.

Thus it appears that the inference drawn in the earlier paper* from a comparison of the Bourdon and the Tait gauges is valid. The breadth of the cycles here was about 40 atmospheres. It is gratifying to note that even the standard atmosphere used was correct to 1 per cent. The present results, however, go further: since the whole of the cyclic motion is in the Bourdon gauge, the indications of the Tait gauge will probably be found very near the truth.

5. My reasons for regarding the mechanism of the gauge as relatively perfect were given elsewhere (*l. c.*); but it is necessary to verify this conclusion by a direct-reading screw-micrometer. Care was taken to fix the axis of the screw

* Phil. Mag. [5] xxx. p. 346.

parallel to the line of motion of the free end of the Bourdon tube, which line was found to be about ·4 centim. long, and inclined at an angle of nearly 45° with the tangent at the free end. The long slender conoidal plug, at the end of which these measurements were made, was about 10 centim. long. Of the two series given in Table II., the first shows some convexity upward in the on march, where the mean factor is ·000362 cm./atm. The data of the off march show distinct convexity downward. Thus the curves form a cycle whose mean breadth is 40 atmospheres, agreeing substantially with § 4. The data of the second series, which show rather better agreement among themselves, in other respects corroborate the first series throughout. The factor is ·000361 cm./atm. Many other measurements both within 500 atmospheres and 1000 atmospheres were made, from which the absence of cycles in case of the smaller interval was again manifest.

The bow-shaped cycles obtained in the present and the earlier paper* are therefore cases of actual hysteresis. I venture to regard the phenomenon as depending on the occurrence of volume-lag in those parts of the tube which are directly influenced by pressure. In other words, the molecules of the metal near the inside of the Bourdon tube pass from the original to a second molecular state, in proportion as a certain pressure P is approached and exceeded; whereas these molecules pass from the second state back to the first again, in proportion as pressure falls below a certain other datum p, where $P > p$. Tables I. and II. show that P must lie somewhere between 500 atm. and 1000 atm., whereas p may lie below 300 atmospheres. Here, therefore, is a phenomenon very similar to the effect of pressure on an under-cooled liquid †.

* Phil. Mag. [5] xxx. p. 344 *et seq.* (1890). See plate x.

† Two other possible explanations of the cyclic changes may be noted. In the first place it is conceivable that the Bourdon tube is hotter during the off march than during the on march. To test this directly it would be necessary to submerge the tube in a water-bath, which is scarcely feasible without impairing the mechanism. I hold this explanation improbable; for if it were true, the comparison within 500 atmospheres should show a cycle proportional in magnitude to the cycle for the interval 1000 atmospheres, which it does not. Again, cycles should quite vanish on long waiting (five minutes were allowed per observation in my earlier work), which they do not. The other explanation seems equally improbable. There may be two figures of equilibrium of the Bourdon tube, one corresponding to low pressure, the other to high pressure: and the figure of labile equilibrium through which the tube passes from the first to the second may be maintained over a relatively large interval of pressure.

6. *The Tait Gauge.*—In Table III. I give two series of cyclic comparisons of the Tait gauge with the Amagat manomètre. The plan of work is similar to that described in § 3. Readings were made in triplets. An interval of two minutes was allowed for cooling after each step of compression. The Tait gauge used is the same to which my earlier observations apply*. The interval of comparison is 1500 atmospheres. At the end of Table III. a short *résumé* of the factors (cm. atm.), corresponding to consecutive pressure-intervals, is given.

TABLE III.—Cyclic Comparison of the Tait Gauge (steel tube) with the Amagat Manomètre.

Tait.	Amagat.	Tait.	Amagat.	Tait.	Amagat.
cm.	atm.	cm.	atm.	cm.	atm.
12·65	1	40·72	786	58·58	1294
21·05	248	31·92	539	65·42	1481
20·73	239	31·57	530	64·05	1437
29·35	487	22·44	271	62·50	1398
28·75	468	22·49	272	62·00	1384
40·80	804	13·05	1	58·50	1289
39·72	768	12·85	1	58·15	1277
51·05	1087			49·49	1038
50·16	1059			49·28	1022
59·20	1305	12·90	0	40·45	785
57·80	1266	21·30	246	40·23	780
64·90	1460	20·95	236	29·86	489
63·98	1432	30·17	498	29·50	480
63·30	1414	29·25	484	20·01	210
62·50	1394	38·82	743	20·06	209
57·20	1247	38·09	724	12·85	−1
56·65	1230	50·14	1057	12·93	−1
49·05	1020	49·10	1033		
41·00	796	60·19	1335		

Factors of the Tait Gauge. Mean Factor ·03596 cm. atm.

Series.	Pressure-interval.	Factor.	Means on and off.	Series.	Pressure-interval.	Factor.	Means on and off.
atm.	cm./atm.	cm. atm.			atm.	cm./atm.	cm. atm.
I., on ...	200 to 1100	·03580		II., on...	200 to 1000	·03544	
I., on ...	500 to 1300	3640	·03628	II., on...	500 to 1300	3602	·03590
I., on ...	800 to 1500	3664		II., on...	700 to 1500	3625	
I., off ...	800 to 1400	·03595		II., off...	800 to 1400	·03594	
I., off ..	500 to 1200	3577	·03576	II., off...	500 to 1300	3591	·03591
I., off ...	300 to 1000	3555		II., off...	200 to 1000	3579	

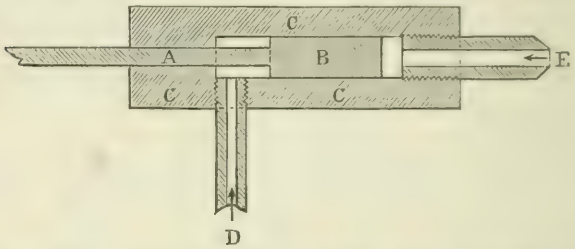
* This Magazine, [5] xxx. p. 344, § 18 (1890). Gauge No. 1.

7. Table III. substantiates the general inferences of § 4. In the first series, above 300 atm. on, the data make up a straight line. Between 0 and 300 atm., on, the registration of the Tait gauge is too high, being more in error as the pressure-zero is approached. In the off series all the points lie on a straight line excepting the zero, which is 10 atm. too high on the Tait gauge. Thus the locus consists of two straight lines converging at 1500 atm., and the cyclic character in § 3 does not appear. In the second series these results are sustained, though the off march returns in the line of the on march. As a whole, therefore, the observations lie on a very flat curve, which above 300 atm. passes into a straight line. It is difficult to conjecture the cause of this curious low-pressure discrepancy, in consequence of the number of minor errors which may be encountered. Possibly the rise of temperature of a liquid, per 100 atm. of adiabatic compression, may decrease with increasing pressure, seeing that at low pressures compressibility is relatively large. Table III. shows, finally, that the mean factor derived from all the data is ·03596 cm./atm. If this be increased ·4 per cent. to allow for the temperature of the mercury column of the manomètre, the more correct value is ·0361 cm./atm. In my former paper* the results were ·0360 to ·0369, showing that my empiric standard atmosphere must have been less than 2 per cent. in error. It is altogether probable that this difference of factor is the result of the excessive use and abuse to which the Tait gauge was put during the intervening nine months. Indeed I believe the residual errors of Table III. to be due rather to unavoidable fluctuations of the temperature of the water-jacket than to thermal effects of compression or viscosity of metal. For this reason I doubt whether any permanent expansion of the metal for the range 1500 atm. has been measured.

8. *Summary.*—In the attempt to carry these comparisons above 2000 atm., I ruptured the stout tube which coupled the compressor and the manomètre. The above work, however, shows conclusively that the Tait gauge may be perfected so as to be available for precise measurement. It is perhaps permissible to indicate the way in which I am endeavouring to do this here, since many of the experimental contrivances involved have already been tested. Thus far the most annoying difficulty is encountered in maintaining the temperature of the water-jacket sufficiently constant. A point of progress will be gained when the whole gauge (excepting the capillary

* Phil. Mag. [5] xxx., Table IV., p. 345 (1890). In this table read $10^2 \times$ cm. atm. instead of cm./atm.

tube) is constructed of metal. Furthermore, choice must be made of as thin-walled a steel measuring-tube as possible, in order that the volume-increase due to pressure may be large relatively to the simultaneous fluctuations of temperature. This can be accomplished by connecting the Tait gauge and the compressor by an *interposed piston libre*. In the annexed diagram let A B be the cylindrical piston, consisting of a



single piece of which one end is larger in diameter than the other*. Let this piston fit the hollow cylinder, C C C, accurately, so as to be capable of motion to and fro, or of rotation, with the minimum of friction. Let the tube D be in connexion with the compressor, the tube E with the Tait gauge, and let the whole apparatus be filled with oil (§ 1). Then it is clear that exceptionally high pressure acting at D can be counterbalanced by relatively low pressure at E. Hence a Tait gauge reading to only 1000 atm. may be made to indicate pressures two, three, or many times as large as this, by selecting a suitable size of piston: and hence an exceptionally thin-walled steel tube may be inserted in the gauge.

I am far from underestimating the importance of Amagat's manomètre as a standard instrument leading at once to absolute results: but it is certainly uncomfortable to be obliged to make readings on a column 4·6 metres high even under favourable circumstances. Nor would it conduce to convenience and certainty if the registration were made electrically. On the other hand, in the case of the Tait gauge, the pressures are read off on a horizontal tube about one metre long, and as far as 2000 atm., without pistons libres, and therefore quite without unavoidable leakage† and continually decreasing pressure.

* My colleague Dr. William Hallock devised other high-pressure apparatus acting on the above principle, some time ago.

† Regarding high-pressure gauges rigorously free from leakage, let me say that I have the apparatus ready for expressing pressure in terms of the isothermal diminution of the electric resistance of pure mercury. *Cf.* American Journal, xl. p. 219 (1890).

XLVIII. *On the Calculation of the Coefficient of Viscosity of a Liquid from its Rate of Flow through a Capillary Tube.* By L. R. Wilberforce, *M.A., Demonstrator in Physics at the Cavendish Laboratory, Cambridge**.

In the method ordinarily employed for calculating the coefficient of viscosity of a liquid from observations upon its rate of transpiration under a known pressure through a capillary tube of known dimensions, it is assumed as a first approximation that the character of the motion at all sections of the tube is the same, and that the motion of the fluid outside the tube can be neglected. Thus, to this approximation, all the energy supplied to the liquid is supposed to be converted into heat within the tube.

If greater accuracy is aimed at, it will therefore be necessary to apply corrections on account of (1) the motion of the fluid outside the tube, and (2) the difference of character of the motion within the tube at points near its ends from that at points remote from them.

The second of these causes seems hitherto not to have been considered; but a value for the correction necessitated by the first cause was investigated by Hagenbach (Pogg. *Ann.* cix. 1860), who noticed that a part of the energy supplied still existed in the issuing fluid as kinetic energy, and that a deduction on this account must be made from the whole energy given to the liquid before it could be equated to the energy expended within the tube. The validity of the assumption upon which he proceeds is, however, very doubtful; but before discussing this I wish to point out an error in the method which he has employed in calculating his correction.

Let ρ be the density of the liquid, r the radius of the tube, z the distance of a point from the axis of the tube, and ζ the velocity at that point; then we shall begin by assuming that everywhere in the tube, even at the end from which the fluid issues,

$$\zeta \propto (r^2 - z^2);$$

or, if v denotes the mean velocity of the fluid,

$$\zeta = \frac{2v}{r^2}(r^2 - z^2).$$

* Communicated by the Author.

Then the kinetic energy carried out by the issuing fluid per unit of time is

$$\int_0^r \rho\, 2\pi z\, dz \,.\, \zeta \times \frac{\zeta^2}{2} = \pi\rho r^2 v^3.$$

Let the transpiration take place under the pressure due to a column of the liquid of height h, then Hagenbach's reasoning is as follows:—If there were no fluid friction, and the flow took place under the pressure due to a height h', the velocity of efflux would be $\sqrt{2gh'}$, and the kinetic energy leaving the tube per second would be $\pi\rho \frac{r^2}{2}(2gh')^{\frac{3}{2}}$; *hence* we must correct h by the subtraction of a quantity h' given by the equation

$$\pi\rho \frac{r^2}{2}(2gh')^{\frac{3}{2}} = \pi\rho r^2 v^3,$$

whence

$$h' = \frac{1}{\sqrt[3]{2}} \frac{v^2}{g}.$$

This reasoning is clearly fallacious; for the pressure which must be applied to produce a certain amount of kinetic energy per unit time will depend upon the work done by the pressure in that time, *i. e.* upon the volume of fluid issuing; and this volume in the actual case differs from that in the ideal case considered by Hagenbach.

The correct reasoning from the same assumptions is as follows:—The volume of fluid which actually flows through the tube under a pressure due to the height h is, per unit of time, $\pi r^2 v$. The energy supplied to this is therefore $\pi r^2 v\, gh\rho$, and the kinetic energy which it possesses on issuing is $\pi\rho r^2 v^3$: hence the energy converted into heat within the tube is $\pi r^2 \rho v g\left(h - \frac{v^2}{g}\right)$. Thus the head h must be corrected by subtracting from it $\frac{v^2}{g}$ instead of $\frac{1}{\sqrt[3]{2}} \frac{v^2}{g}$.

Hagenbach tested his method of correction by applying it to a set of very rough experiments of his own, made at slightly varying temperatures, and in which, as it appears, the liquid was allowed to issue into the air, so that there was a capillary back-pressure of varying magnitude. The reduced results which he obtained agreed very badly when the cor-

rection became at all sensible, and he accounted for this by supposing that the flow in the tube became turbulent at the higher velocities; but this could not have been the case, as the mean velocity was, in every experiment except the last one, well below the critical value at which linear motion ceases to be resumed upon disturbance. If instead of his correction we use the modified form which we have shown should replace it, the results are distinctly better, as will be seen from the subjoined Table, which gives the values in C.G.S. units of the coefficient of viscosity of water deduced from Hagenbach's experiments.

Employing Hagenbach's correction.	Employing the larger correction.	Temperature.
		°
·0101	·0101	19·7
·0101	·0100	19·7
·0100	·0099	19·7
·0093	·0092	20·2
·0098	·0098	20·4
·0099	·0098	20·2
·0101	·0100	19·8
·0101	·0099	20·1
·0101	·0100	19·6
·0103	·0100	19·6
·0104	·0100	19·5
·0110	·0105	19·7
·0118	·0110	19·7
·0118	·0106	19·5
·0126	·0109	19·6
·0138	·0109	19·5

Hagenbach also applied his correction to a number of experiments of Poiseuille's. We shall see later that here also it gives in its modified form results which are slightly less inconsistent.

It is clear, however, that in the application of this method of treatment to experiments such as those considered above, we tacitly assume, in calculating the value of h, that the pressure over the whole of that end of the tube from which the liquid issues may be taken as sensibly constant and of the same value as if there were no motion; an assumption unsupported by probability.

The complete discussion of the problem before us is impossible in the absence of a solution for this case of the equations of motion of a viscous fluid, but some considerations upon

the form in which the necessary corrections must present themselves may be of service.

Osborne Reynolds (Phil. Trans. 1883) has experimentally shown that, in a tube of given diameter D, if the mean velocity is not greater than a certain critical value the motion of a fluid at points not very near the ends (*i. e.* about 120 diameters off, in his experiments) settles down into the state which we have hitherto assumed to exist throughout. He refers to these experiments in a later paper (Phil. Trans. 1886), and there gives $\frac{r\rho D}{\mu}=1400$, μ being the viscosity of the liquid, as an equation from which to determine the critical velocity; but from the experimental results given in the earlier paper it would appear that the number should be 2000.

It follows that if the tube be long compared with its diameter, and if the mean velocity be below its critical value, both of which conditions we shall assume, the motion near each end of the tube both within it and outside will depend only upon the mean velocity and not upon the length of the tube.

We shall suppose that the fluid flows from a vessel into the tube, and from the tube into a mass of fluid of the same kind in another vessel; and that when we investigate the effect of a change in the diameter of the tube, we change the dimensions of the vessels in the same proportion, and so arrange the tube with respect to them that the whole system shall remain similar to itself, the length of the tube alone excepted; then, from the form of the equations of motion of a viscous fluid, we deduce that the character of the motion at similar points in the different experiments will be a function of $\frac{r\rho D}{\mu}$ only.

We may consider that this motion of unknown character exists in the vessels and in the tubes up to distances of $D\times f_1\left(\frac{r\rho D}{\mu}\right)$ and $D\times f_2\left(\frac{r\rho D}{\mu}\right)$ from the ends, and that in the rest of the tube the distribution of velocity is the normal one. Since for the case of similar fluid systems moving similarly the dissipation function is proportional to *volume* × *coefficient of viscosity* × (*gradient of velocity*)^2, we have for the energy dissipated per unit time in the vessels and ends of the tube,

$$D^3\times\mu\times\left(\frac{r}{D}\right)^2 F\left(\frac{r\rho D}{\mu}\right).$$

The rate at which energy is dissipated in the rest of the tube

per unit length is easily proved to be $8\pi\mu v^2$, and the rate at which energy is supplied is $g\rho hv\frac{\pi D^2}{4}$. Hence we obtain, if l is the length of the tube,

$$g\rho hv\frac{\pi D^2}{4}=8\pi\mu v^2\left[l-D\left\{f_1\left(\frac{vD\rho}{\mu}\right)+f_2\left(\frac{vD\rho}{\mu}\right)\right\}\right]+\mu v^2 D\,F\left(\frac{vD\rho}{\mu}\right),$$

which may be written

$$h=\frac{32\mu lv}{g\rho D^2}+\frac{\mu v}{g\rho D}\psi\left(\frac{vD\rho}{\mu}\right),$$

or

$$h=\frac{32\mu lv}{g\rho D^2}+\frac{v^2}{g}\phi\left(\frac{vD\rho}{\mu}\right).$$

If the walls of the vessels are everywhere at a distance from the ends of the tube which is great compared with the diameter of the tube, it may be expected that the function ϕ will be practically independent of the shapes of the vessels. In any case, from the results of two experiments made with vessels proportioned to the diameters of the tubes, and with pressures so chosen that vD is the same in both, we can eliminate the correction. In particular, using the same vessels in the two experiments and tubes of the same diameter but of lengths l_1 and l_2, if the heads corresponding to a mean velocity v be h_1 and h_2, we have

$$\mu=\frac{g\rho D^2(h_1-h_2)}{32\,v(l_1-l_2)}.$$

The large number of observations made by Poiseuille upon water at a constant temperature, and the close agreement which, according to his method of exhibiting the results, appeared to exist between those of his first series of experiments, led me to apply the above methods of calculation to most of the data which his second series of experiments furnish. It would be wearisome to tabulate the issues of the calculations at length; the various results obtained with the same piece of tube seemed on the whole to point to the simple correction of h by $\frac{v^2}{g}$ as being appropriate for a considerable range of velocity; but they were not very consistent, and the results obtained with different portions of tube, even those which were cut from the same piece, and about the ratio of

whose diameters there was in consequence little uncertainty, were quite irreconcilable.

In order to compare the different experiments, a curve in which r was the abscissa and $\frac{h}{r}$ the ordinate was plotted for each tube. Then, considering the curves for two tubes of different lengths but the same diameter, and assuming that no appreciable effect was produced by the ends occupying different positions with regard to the vessels into which they opened, the ordinates for the same abscissa should have differed by a constant quantity; and this quantity, multiplied by the square of the diameter of the tubes and divided by the difference in length, should have been equal to $\frac{32\mu}{g\rho}$, *i. e.* to a constant multiple of the coefficient of viscosity.

The values thus deduced for the coefficient were very discordant; for example, those deduced from Poiseuille's tube (A) varied from $\cdot000403\times\frac{g}{32}$ to $\cdot000445\times\frac{g}{32}$.

These differences were very large indeed when compared with the concordance which seemed to exist between the experiments of the first series; but upon examination of these, it appeared that their discrepancies were in reality almost as great, and that Poiseuille's final comparison was only one between a comparatively small number of results whose agreement was quite fortuitous. It was in fact found that the coefficient of viscosity deduced from the experiments of the first series by the ordinary uncorrected formula varied from $\cdot000409\times\frac{g}{32}$ to $\cdot000437\times\frac{g}{32}$; and as here these differences occurred even when the velocity was so low that the correction must have been quite insensible, it became evident that the errors of experiment were too large to allow the results to be available for my purpose.

I had reached this stage of the investigation at the beginning of the present year, and was hoping to carry out some experiments of the same general nature as Poiseuille's in order, if possible, to determine in some simple cases numerical values for the function $\phi\left(\frac{v\rho D}{\mu}\right)$, when my attention was called to a statement by Gartenmeister, in the number of the *Zeitschrift für Physikalische Chemie* published on December 31st, that Prof. Finkener of Berlin had suggested to him as preferable to Hagenbach's correction the same greater value which I

have shown above ought, if we follow Hagenbach in his assumptions, to be substituted for it. Gartenmeister gave no indications of the method by which this result was obtained, nor of the reasons which rendered it preferable; but stated that a paper by Prof. Finkener on the whole subject would shortly appear. Under the circumstances, therefore, it seemed best to wait for the results which he has obtained before trying to proceed with the question.

Another attempt to apply to the numbers obtained by Poiseuille in his second series of experiments a correction for the kinetic energy given to the fluid was made by Osborne Reynolds, apparently in ignorance of Hagenbach's work on the subject, in the paper already referred to (Phil. Trans. 1883). The correction which he employed was $1{\cdot}505\,\frac{v^2}{2g}$, and was thus slightly smaller than Hagenbach's, whose value was $\cdot 7937\,\frac{v^2}{g}$. The authority for this correction appears to be Weisbach; but as the experiments from which he deduced it were made with tubes 1 to 4 centim. in diameter and only 3 to 12 centim. long, and the head of water used varied from 9 to 24 inches, it is clear that the velocities were so far above the critical velocity as to make the results inapplicable to this case. Indeed, Weisbach mentions that experiments with narrower tubes were found to give a different result.

Osborne Reynolds considered that when the above correction was applied, Poiseuille's results became consistent; but the correction $\frac{v^2}{g}$ gives rather better results in all the experiments of the second series which I have examined, while the discordances which any of these corrections introduce among the seeming agreements of the first series are not sufficiently different to help us in deciding between them.

The subjoined Table gives specimens of the results obtained. It indicates the relative merits of the various corrections, and at the same time shows the inapplicability of the numbers obtained by Poiseuille to the method of calculation suggested in this paper.

	$\frac{h}{v}$	$\frac{v}{g}$	$\frac{h}{v}-\frac{1}{\sqrt{2}}\frac{v}{g}$	$\frac{h}{v}-\cdot7525\frac{v}{g}$	$\frac{h}{v}-\frac{v}{g}$	$\left(\frac{h}{v}-\frac{v}{g}\right)\frac{D^2}{l}$
Tube A. $l=5{\cdot}11$ cm. D= ·01416 cm.	10·90	·01	10·89	10·89	10·89	·000427
	10·91	·02	10·90	10·90	10·89	
	10·86	·02	10·84	10·84	10·84	
	10·90	·05	10·86	10·86	10·85	
	10·89	·10	10·81	10·80	10·79	
Tube A. $l=1{\cdot}575$ cm. D= ·01417 cm.	3·421	·010	3·413	3·414	3·411	·000435
	3·465	·020	3·449	3·450	3·445	
	3·457	·039	3·426	3·428	3·418	
	3·460	·059	3·413	3·417	3·401	
	3·476	·077	3·414	3·419	3·399	
	3·554	·151	3·433	3·442	3·403	
	3·706	·289	3·475	3·493	3·417	
Tube F. $l=38{\cdot}38$ cm. D= ·06533 cm.	3·930	·003	3·927	3·927	3·927	·000437
	3·920	·008	3·914	3·914	3·912	
	3·897	·017	3·883	3·884	3·880	
	3·869	·036	3·840	3·842	3·833	
	3·931	·051	3·890	3·893	3·880	
	3·899	·086	3·830	3·835	3·813	
	3·993	·133	3·887	3·895	3·860	
	3·992	·267	3·778	3·795	3·725	
Tube F. $l=9{\cdot}9725$ cm. D = ·06533 cm.	1·040	·008	1·034	1·034	1·032	·000442
	1·027	·016	1·014	1·015	1·011	
	1·043	·032	1·017	1·019	1·011	
	1·072	·063	1·022	1·026	1·009	
	1·137	·118	1·043	1·050	1·019	
	1·174	·172	1·036	1·047	1·002	
	1·233	·214	1·062	1·075	1·019	
	1·490	·356	1·205	1·227	1·134	
Tube F. $l=2{\cdot}600$ cm. D = ·06546 cm.	·301	·027	·279	·281	·274	·000452
	·326	·051	·285	·288	·275	
	·377	·089	·306	·312	·288	
	·444	·152	·322	·332	·292	
	·551	·245	·355	·370	·306	
	·637	·318	·383	·403	·319	

According to Hagenbach $\frac{h}{v}-\frac{r}{\sqrt[3]{2g}}$ should be constant for the same portion of tube; according to Osborne Reynolds $\frac{h}{v}-\cdot7525\frac{r}{g}$ should be taken. If the correction to be applied to h were $\frac{r^2}{g}$, then $\frac{h}{v}-\frac{r}{g}$ should be constant for the same tube, and $\left(\frac{h}{v}-\frac{r}{g}\right)\frac{D^2}{l}$ should be a constant multiple, $\frac{32}{g}$, of the coefficient of viscosity.

XLIX. *Note on the Electric Conductivity of Hot Gases.* *By* Dr. Svante Arrhenius*.

THE following lines have reference to Prof. J. J. Thomson's letter in the Philosophical Magazine for February 1891, p. 135. The question at issue between Prof. Thomson and myself is whether gaseous hydrochloric, hydrobromic, and hydriodic acids (and, still more, chlorine, bromine, and iodine) conduct electricity electrolytically at high temperatures, or only conduct in consequence of dust-particles suspended in them. Prof. Thomson's view is that the hydrochloric-acid molecules (HCl) decompose partially at high temperatures into atoms of hydrogen and chlorine (H and Cl) which are charged with electricity, positive or negative, according to Faraday's Law, *i. e.* are charged with 96 coulombs per milligram-equivalent. Crafts† has shown that such a decomposition, which would be recognized by its effect on the vapour-density, does not take place at the temperature of Prof. Thomson's experiments (yellow heat, about 1100° C.). It is conceivable, however, that very little decomposition might suffice to cause the electrolytic conduction; and so we will assume in the meantime that there is a slight dissociation of HCl into $\overset{+}{H}$ and $\overset{-}{Cl}$, not measurable by other means. It must be clearly understood that this dissociation is assumed for the exclusive purpose of explaining the conductivity, and is not, as one might imagine from Prof. Thomson's account, suggested by other circumstances.

If such a dissociation takes place, it need not in any way be (perceptibly) dependent on the quantity of hydrogen (H_2) present. The equilibrium is one between $\overset{+}{H}$, $\overset{-}{Cl}$, and HCl; just as it is between PCl_3, Cl_2, and PCl_5 in Prof. Thomson's example. Whether the presence of H_2 will affect the quantity of $\overset{+}{H}$ (and $\overset{-}{Cl}$) or not, depends entirely on whether there is any interaction between H_2 and $\overset{+}{H}$ (or $\overset{-}{Cl}$) of sufficient extent to have an appreciable effect on the above equilibrium. This certainly cannot be asserted *à priori*, but must be considered an accessory hypothesis introduced to explain Prof. Thomson's observation that the conductivity of HCl is diminished by the presence of H_2.

* Communicated by the Author.

† *Comptes Rendus*, xc. p. 311:—"On a trouvé dans les expériences suivantes une densité normale pour l'acide chlorhydrique à la plus haute température du fourneau"—*i. e.* 1400°–1500° C.

Now it seems to me that the following explanation of Prof. Thomson's experiments is much more plausible. In the cases under discussion he was always able to prove the presence of free halogen—in the above example, of free chlorine (Cl_2)—by the reaction of the heated gases with potassium iodide and starch. It must be expressly stated that this reaction is for the *molecules* Cl_2, Br_2, and I_2, and not for the ions $\bar{Cl}$, $\bar{Br}$, and $\bar{I}$, which in aqueous solution do *not* exhibit the reaction. If Prof. Thomson, then, is of opinion that he has proved the presence of $\bar{Cl}$ in the heated hydrochloric-acid gas, his conclusion cannot be accepted. On the contrary, it may easily be shown that the two charged ions of an electrolyte cannot be separated from each other in appreciable quantity (about 10^{-5} milligram-equivalents) by mechanical means; for the separation of 10^{-10} milligram-equivalents of $\bar{Cl}$ would be sufficient to charge a sphere of 10 centimetres radius to 900 volts—an electromotive force which would certainly suffice to bring the $\bar{Cl}$ back to the $\dot{H}$.

Prof. Thomson has only thus proved the presence of free chlorine (Cl_2) in the heated hydrochloric acid of his experiments. This may be accounted for in two ways. Either HCl decomposes at a high temperature so as to produce a state of equilibrium between H_2, Cl_2*, and 2HCl; or—and this alternative seems to me much more probable—oxygen (air) may have been present in the hydrochloric-acid gas, and have liberated chlorine with formation of water. We are informed that the experiments with sulphur and hydrogen sulphide were conducted in an atmosphere of nitrogen; but no such indication is given with respect to the other gases (HCl, NaCl, KCl, NH_4Cl, KI, and HI). In either case the quantity of free chlorine (Cl_2) would be diminished by the presence of hydrogen. Now it is quite likely that the free halogen would favour convective conduction, if such is assumed in Prof. Thomson's experiments. Crafts tells us (*loc. cit.* p. 186) that his chlorine attacked platinum with violence, and the same is probably true of the other halogens, although perhaps in their case the action is less intense. It is therefore easily conceivable that platinum would be dispersed as fine particles more readily in an atmosphere containing Cl_2, than in an atmosphere where chlorine gas is absent; and it is owing to the transport of electricity by

* Cl_2 does not decompose perceptibly into 2Cl at 1100°—Crafts.

means of such fine particles that convective conduction takes place.

That Prof. Thomson has really had to do with convective conduction (for the most part) in his experiments seems to me apparent from several circumstances. Convective conduction is favoured relatively to electrolytic by low temperatures and high E.M.F.'s. Now Prof. Thomson worked at a temperature 100° lower, and with an E.M.F. 60 times greater, than I employed in my experiments; in some of which, even, convective conduction played a considerable part. Again, conduction by means of solid particles obeys Ohm's Law; while electrolytic conduction (with E.M.F. above 1 Dan.) is characterized by large deviations from this law. Prof. Thomson found in his experiments (with high E.M.F.) that Ohm's Law was obeyed; consequently the conduction was probably convective, as it was in my experiments with salts of magnesium, calcium, and strontium.

Prof. Thomson's results are thus explained very naturally by the following two assumptions:—

1. That, as in the analogous researches of Becquerel, Blondlot, and Wiedemann and Ebert, a preponderating non-electrolytic conduction through dust-particles took place.

2. That free halogens, like chlorine in the experiments of Crafts, had a corrosive influence on the platinum vessel and electrodes, whereby the formation of fine particles (and consequently the convection) was increased.

The experiments with mercury vapour (Hg) show in the most decisive manner that Prof. Thomson's view of the activity of atoms in gaseous conduction is untenable: for it is in the highest degree improbable that the opinion, grounded on so many circumstances (*e.g.* vapour-density, specific heat), that gaseous mercury-molecules consist of single atoms, will be sacrificed in order to save Prof. Thomson's theory.

Finally, Prof. Thomson refers to my query: "Who can prove that iodine vapour decomposes entirely into ions? It might dissociate into uncharged atoms." This question Prof. Thomson answers by asking two others connected with it; and these, as it chances, are very easy to dispose of. The first is: "If the atoms of a gas (I_2) can be without charge, why cannot those of a salt (NaCl) in solution?" If a measurable quantity of uncharged atoms (Na and Cl) were present in a solution of NaCl, then, as in the case of ordinary dissociation (*e.g.* of $K_2Al_2S_4O_{16}$ into K_2SO_4 and $Al_2S_3O_{12}$), we should be able to separate these components by diffusion (dialysis). Now it is one of the most firmly established facts that, in spite of numberless experiments, this

has never been done in a single case with salts. There consequently exist no uncharged atoms in a salt solution. This purely empirical proof can evidently not be extended to the case of I_2: but there is a great difference between the two instances. It is easy to imagine that the two ions of a salt (Na and Cl from NaCl), which are in other respects so different from each other, should also be the bearers of different kinds of electricity; but it is difficult to admit that atoms otherwise completely identical (I and I from I_2) should assume, or possess, opposite electrical charges; for complete symmetry prevails in the molecule. Prof. Thomson's experiments on the feeble conductivity of iodine vapour compared with mine on cæsium chloride (CsCl), yield, besides, sufficient proof that the iodine atoms are *not* charged in measurable degree according to Faraday's Law.

The second question drops of itself when the first has received the above answer. It runs: "If we admit the existence of uncharged atoms (in solution), why should there be any connexion between electric conductivity and osmotic pressure?" Since our experience shows us that there are no uncharged atoms in salt solutions, the connexion Prof. Thomson mentions must obtain. With regard to Cl_2, Br_2, and I_2, we have no such experience as for salt solutions: and Prof. Thomson's assertion that the conductivity of these gases stands in connexion with their dissociation at high temperatures, *i. e.* with their gaseous pressure, is as yet entirely without foundation, either theoretical or experimental.

I share with Prof. Thomson the opinion that, after his two questions are disposed of, my own query is so likewise, and trust that the facts brought forward in the preceding pages will supply sufficient material to any one for its unequivocal answer.

Upsala, 23rd February, 1891.

L. *On the Reduction of the Results of Experiments with special reference to the Hydrate-theory of Solution. By* Sydney Lupton, *M.A.**

THE problem of finding a formula to express quantitative experimental results is, partly owing to unavoidable errors of observation, by no means an easy one, and has severely taxed the powers of mathematicians. Experimentalists are very apt to attribute impossible accuracy to results on which they have expended much care and time, and in the

* Communicated by the Author.

hurry of modern life are apt to omit the test of accuracy afforded by obtaining the same results by several different methods. Thus long rows of figures are frequently given which have in reality no experimental basis to rest upon. On the other hand, mathematicians obtain formulæ which require experimental results of unattainable accuracy, and frequently immense arithmetical labour in the course of which the experimentalist is led into bewilderment and error.

There are only three possible methods of finding an equation to connect two or more physical quantities, of which one has been recently applied in a manner open to very grave suspicion.

(i.) By deduction from a general law assumed to connect the phenomena the form of the required function is obtained and the constants are then determined by experiment. Too little is known about the ultimate constitution of matter to allow of the safe application of this method in the cases which ordinarily occur in physics and chemistry. It is, however, used not unfrequently in astronomy and practical mechanics, *e. g.* in determining heights by the fall of the barometer, and the variation in gravity with latitude.

(ii.) In the graphical method the experimental results are plotted on a sheet of paper or metal, and a curve drawn through these points is assumed to give the most reliable expression for the general law. The problem of drawing a curve through any given points is essentially an indeterminate one, hence the following further assumptions are generally made :—(*a*) the simplest curve (*i. e.* with the fewest changes of curvature) which *fairly* fulfils the given conditions is to be chosen ; (*b*) nearly an equal number of experimental results should lie on each side of each portion of the curve.

No one can deny the great value of this method in all cases in which minute accuracy is not required. Thus it gives a ready solution of the efficiency of engines and machines, the volume of earthwork, and the best shape of roof and bridges ; but when it is applied to the solution of certain theoretical questions, it is apparently pressed at times beyond its power.

Regnault made use of a copper sheet divided into small squares, in which the intersection of the experimental ordinate and abscissa was drawn by a special dividing-engine. Among these points a curve was drawn by the "free hand" and engraved.

Experimentalists now prefer squared paper. In some of French manufacture a sheet is divided into 1,000,000 millimetre squares by dotted lines, with five dots to the millimetre. In the middle part of such a sheet one part in 2500 can be

measured, though of course the accuracy is greater at one end and less at the other. A wooden or steel, occasionally backed by lead, lath is bent between the points and the curve drawn along it. With sufficient trouble an arithmetical result can be carried to any required degree of accuracy. But it is far otherwise with a graphical one: probably about $\frac{1}{1000}$ is the limit of careful work in this case. The value of π has been calculated by two independent individuals to 500 figures; by careful drawing, Stanley Jevons could obtain it only to $\frac{1}{546}$. Very careful use of the ruler and compasses is required to obtain the sixth figure in the ratio of the diagonal to the side of a square, while in a few minutes any one may convince himself that $\sqrt{2}=1{\cdot}41421\ 35623\ 73\ldots$.

Mr. Pickering gives no details as to the method used in drawing his curves, but mentions one hundredth of an inch as about the limit of accuracy; it is therefore a little astonishing to find him dealing with an abscissa of 50·06998 parts per cent. of real acid, and a corresponding ordinate of 1·404296 grams per cubic centimetre. Even the latter value would assume an accuracy of measurement of $\frac{1}{100}$ inch in 14,042 inches, or 390 yards: and of course he has to substitute another method.

Two points are specially worthy of notice:—

Even those who depend most upon this method, including Mr. Pickering, allow that a strong personal element is introduced, since two observers might take different views as to the form of curve which would most fairly represent the results; hence considerable care and practice are requisite before it can be safely used. For this reason alone, if an arithmetical process can be found which will give the same results in all hands, it ought to be preferred.

Secondly, according to Mr. Pickering, when the steel lath he used is bent by the two hands it is really fixed in four points. He says it "does not form a curve of any particular nature, and does not necessarily give a curve which will differentiate eventually into a straight line; but if the experiments form a figure on to which the bent steel *cannot* be fitted, that figure certainly does not consist of a single parabolic curve" (Journ. C. S. 1890, p. 68).

A chemist may certainly be excused if he avoids the mathematics of a flexible plate deformed by four pressures; but does not the practical solution approximate to choosing four points such that the curve drawn through them may lie evenly among the experimental points? Through four points a curve of the second degree can be drawn in a variety of ways, since a fifth point is required to determine a definite curve.

When the terms of an equation of the second degree are differentiated, and the differential $\frac{dy}{dx}$ is replaced by a new ordinate z suppose, an equation of the first degree representing a straight line is obtained. Hence the hydrates of sulphuric acid are apparently made to depend upon the flexibility of the steel lath used.

(iii.) The empirical method—the form of the equation is guessed at, often by the aid of the plotted curve; the constants are determined from the experimental results, and the calculated are compared with the observed numbers.

In the great majority of cases in Physics and Chemistry the value of the variant for any value of the variable may be expressed with sufficient accuracy by one or more terms of the equation

$$u_x = \phi(x) = a + bx + cx^2 + dx^3 +$$

where a, b, c, d are constants which may be zero or negative, and must be determined by experiment.

The assumption that $\phi(x)$ can be expanded in ascending powers of x is by no means universally true. In some cases a derived function becomes a constant and the series becomes finite; in other cases some of the differential coefficients become infinite and the series fails, e. g. $e^{-\frac{1}{x}}$ when $x=0$. In some practical cases, as in that of the tension of aqueous vapour, the series required is unmanageable and another equation must be chosen.

Four values of u are determined by widely separated experiments, in one of which, if possible, x is made equal to 0 to determine a; the constants are then solved for by the theory of determinants, or by the method of cross multiplication due to Lagrange, which gives:—

$$b = \frac{\overline{u_1 - a(x_2^2x_3^3 - x_2^3x_3^2)} + \overline{u_2 - a(x_1^3x_3^2 - x_1^2x_3^3)} + \overline{u_3 - a(x_1^2x_2^3 - x_1^3x_2^2)}}{x_1(x_2^2x_3^3 - x_3^2x_2^3) + x_2(x_1^3x_3^2 - x_1^2x_3^3) + x_3(x_1^2x_2^3 - x_1^3x_2^2)};$$

$$c = \frac{\overline{u_1 - a(x_2^3x_3 - x_2x_3^3)} + \overline{u_2 - a(x_1x_3^3 - x_1^3x_3)} + \overline{u_3 - a(x_1^3x_2 - x_1x_2^3)}}{x_1^2(x_2^3x_3 - x_2x_3^3) + x_2^2(x_1x_3^3 - x_1^3x_3) + x_3^2(x_1^3x_2 - x_1x_2^3)};$$

$$d = \frac{\overline{u_1 - a(x_2x_3^2 - x_2^2x_3)} + \overline{u_2 - a(x_1^2x_3 - x_1x_3^2)} + \overline{u_3 - a(x_1x_2^2 - x_1^2x_2)}}{x_1^3(x_2x_3^2 - x_2^2x_3) + x_2^3(x_1^2x_3 - x_1x_3^2) + x_3^3(x_1x_2^2 - x_1^2x_2)}.$$

Were all the results absolutely accurate, the same values for the constants would be obtained whatever experiments were used; but owing to errors of observation the values found differ, and the most probable ones can be obtained by the following method.

Reduce any number of equations to the form

$$u_1 = bx_1 + cx_2^2 + dx_3^3.$$

Multiply each equation by the coefficient of b in it and add all the equations; the resulting "normal equation" when solved gives the most probable value for b. Proceed in the same manner for c and d. Writing X^2 for $x_1^2 + x_2^2 + x_3^2 + \ldots + x_n^2$, we have :—

$$\begin{aligned} u_1x_1 + u_2x_2 + \quad + u_nx_n &= X^2b + X^3c + X^4d, \\ u_1x_1^2 + u_2x_2^2 + \quad + u_nx_n^2 &= X^3b + X^4c + X^5d, \\ u_1x_1^3 + u_2x_2^3 + \quad + u_nx_n^3 &= X^4b + X^5c + X^6d. \end{aligned}$$

The solution of these equations is generally performed by Gauss's method, but at the best is very long and tedious.

The following method is much more simple and convenient, and affords a test of the real value of the equation found.

Subtract each equation from the one below it and divide by $\overline{x_2 - x_1}$, and the similar terms

$$\delta u_1 = \frac{\Delta u_1}{x_2 - x_1} = b + \overline{x_2 + x_1}\,c + \overline{x_2^2 + x_2x_1 + x_1^2}\,d,$$

$$\delta u_2 = \frac{\Delta u_2}{x_3 - x_2} = b + \overline{x_3 + x_2}\,c + \overline{x_3^2 + x_3x_2 + x_2^2}\,d,$$

$$\delta u_3 = \frac{\Delta u_3}{x_4 - x_3} = b + \overline{x_4 + x_3}\,c + \overline{x_4^2 + x_4x_3 + x_3^2}\,d.$$

Subtract again and divide by $x_3 - x_1$ and similar terms,

$$\delta^2 u_1 = \frac{\Delta^2 u_1}{\overline{x_2 - x_1}\ \overline{x_3 - x_1}} = c + \overline{x_3 + x_2 + x_1}\,d,$$

$$\delta^2 u_2 = \frac{\Delta^2 u_2}{\overline{x_3 - x_2}\ \overline{x_4 - x_2}} = c + \overline{x_4 + x_3 + x_2}\,d.$$

Subtract again and divide by $\overline{x_4 - x_1}$:

$$\delta^3 u_1 = \frac{\Delta^3 u_1}{\overline{x_2 - x_1}\ \overline{x_3 - x_1}\ \overline{x_4 - x_1}} = d.$$

Substituting successively in these equations

$$\begin{aligned} d &= \delta^3 u_1, \\ c &= \delta^2 u_1 - \overline{x_3 + x_2 + x_1}\,\delta^3 u_1, \\ b &= \delta u_1 - \overline{x_2 + x_1}\,\delta^2 u_1 + \overline{x_3x_2 + x_3x_1 + x_2x_1}\,\delta^3 u_1. \\ a &= u_1 - bx_1 - cx_1^2 - dx_1^3. \end{aligned}$$

When, as occasionally happens, x_1, x_2, x_3 are in arithmetical progression with a common difference h,

$$\delta u_1 = \frac{\Delta u_1}{h},$$

$$\delta^2 u_1 = \frac{\Delta^2 u_1}{2h^2},$$

$$\delta^3 u_1 = \frac{\Delta^3 u_1}{6h^3}.$$

Owing to experimental error the differences found are never exactly equal, and Mr. J. Hopkinson (Messenger of Mathematics, 1872, ii. p. 65) proposes to add together the various values obtained and take the mean as the most probable value. Though the method has no theoretical basis to rest upon, it is comparatively easy and should give the same results in all hands, while any method of plotting and curve drawing introduces a further series of observations liable to personal error.

There are three great advantages :—

(*a*) The sum of the differences of the observed and calculated values = 0.

(*b*) If the values in the last column of differences regularly increase or decrease, another term must be added to the equation.

(*c*) If the differences are very irregular, there is a want of accuracy in the observations, or the theoretical equation is carried further than the experiments warrant.

If N be the number of observational equations each differencing removes one, so that going as far as $\delta^3 u$ there are really only $N-3=n$ complete equations to deal with. The following separate values must be found from each equation, added together and divided by n.

$$\Sigma x/n, \quad \Sigma x^2/n, \quad \Sigma x^3/n,$$

$$\Sigma u/n, \quad \Sigma \delta u/n, \quad \Sigma \delta^2 u/n, \quad \Sigma \delta^3 u/n ;$$

$$\Sigma(\overline{x_1+x_2} + \overline{x_2+x_3} + \quad \overline{x_n+x_{n+1}})/n = \frac{2\Sigma(x_1+x_n)+x_{n+1}-x_1}{n};$$

$$\Sigma(\overline{x_1+x_2}+x_3+ \quad x_n+x_{n+1}+x_{n+2})/n = \frac{3\Sigma(\overline{x_1+x_n})+x_{n+2}+2x_{n+1}-x_2-2x_1}{n};$$

$$\Sigma(\overline{x_1x_2+x_2x_3}+x_1x_3+ \quad x_nx_{n+1}+x_{n+1}x_{n+2}+x_nx_{n+2})/n =$$

$$\frac{3\Sigma(x^2)+\frac{2}{n}\Sigma\{\overline{x_2-x_1}+\overline{x_3-x_1}\}\Sigma(x)+\frac{1}{n}\Sigma x_2-x_1\,\overline{x_3-x_1}}{n};$$

where mean values must be taken for the differences of x, which are usually small.

These somewhat long preliminaries form a basis for the discussion of the recent application of the graphical method to the theory of solution.

In an account of the nature of solution having special reference to ethyl alcohol (Journ. C. S. 1887, p. 778), Mendeléeff propounded the idea that, if solutions are regarded as strictly definite atomic chemical combinations at temperatures higher than their dissociation-temperatures, the expression for density u as a function of the percentage composition x must be a parabola of the second order, or it may be represented by the general equation

$$u = a + bx + cx^2.$$

Between two definite compounds, which exist in solution, we must expect that the differential coefficient $\frac{du}{dx} = b + 2cx$ will be a rectilinear function of x. This consequence can in the first place be verified by experiment, and secondly gives the means of ascertaining what are the definite combinations existing in solution. The hypothesis has been proved to be correct, and up to this time I have not met with a single exception.

It seems then that Mendeléeff assumed a certain form of equation; collected experimental results, from other observers in many cases, to determine the constants; and found that the equation fairly represented the results of experiments. He then differentiated, replaced the differential coefficient by a new ordinate, plotted the results, and found that they were represented by straight lines. He assumed that the intersection of these straight lines showed a change in the nature of the dissolved substance which could only be the formation of another hydrate.

This method may be valid *if* the experimental results can prove the equation to be absolutely and not only approximately true. Mr. Pickering, however, made use of an entirely different method, and says:—"My conclusions as to the first differential of the densities are in direct opposition to Mendeléeff's" (Journ. C. S. 1890, p. 79); and even more emphatically in Phil. Mag. xxix. p. 133:—"I altogether disagree with Mendeléeff's views as to the nature of the density first differential."

Considering that Mendeléeff's results were not sufficiently numerous or accurate to support such an important conclusion, Mr. Pickering undertook a laborious research on the

hydrates of sulphuric acid and other solutions (Journ. C. S. March 1890; Phil. Mag. 1890, xxix. p. 433), with special reference to the density, expansion, heat of combination, and electric conductivity. While this work was in progress Prof. O. J. Lodge ('Nature,' July 18th, 1889) gave a word of warning to experimentalists on the over-pressure of formulæ, and Arrhenius (Phil. Mag. xxviii. p. 37) severely criticised a preliminary account of Mr. Pickering's methods, pointing out that his equations for sulphuric acid required the introduction of nearly sixty constants, from which anything could be proved.

It is always an ungracious and difficult task to criticise experiments upon which much time and care have been expended, and in this case the difficulty is increased by the omission from Pickering's paper of many experimental details and by the great number and variety of the experiments. To minimize the latter the following remarks will be confined to the density of solutions of sulphuric acid at 28° C., containing from 50 to 38 per cent. of real acid (Table II.), Journ. C. S. 1890, p. 142.

The objections may be conveniently divided into those which impugn the *extreme* accuracy of the experimental results, and those against the mathematical deductions.

Experimental :—

(1) Mr. Pickering's results do not agree with those of Mendeléeff; he says :—"Mendeléeff's values by no means warranted the conclusion that the first differential consisted of straight lines. . . . . The curves required a second differentiation before they yielded a rectilinear figure" (Journ. C. S. 1890, p. 66).

(2) As the mean of eight volumetric determinations starting from pure silver, the acid used was assumed to contain 99·85 per cent. of real acid. It is a little startling in the case of experiments the whole object of which is extreme accuracy to read for the separate values found

99·953	A	99·753	B
·816		·962	
·704		·854	
·857		·897	

with a difference of ·1 per cent. on each side of the mean used.

(3) The thermometer read to ·1 millim. = ·004° C. and the balance weighed to ·0001 gram. The densities were determined in a "piknometer" holding 25 cubic centim., it was apparently of the old form, and a glass plate was placed over the open capillary. The objections to this form of instrument,

which was abandoned by Regnault, are well known; one is that the stopper does not go in to *exactly* the same position when unequally pressed or moistened with different liquids.

(4) Mr. Pickering does not mention any precaution taken to reduce the flask and weights to their true weights *in vacuo*; to remove the oxygen and nitrogen dissolved in the liquid, which might amount to half a cubic centimetre at 10° C., or the air retained between the liquid and the glass. Though he states that ·0002 gram may be taken as the safe limit of error, this is about the weight of a sixth of a cubic centimetre of air.

The question of the value of the method is of far greater importance than that of any individual series of experiments.

(1) Mr. Pickering complains that his method has been persistently misunderstood. "It does *not* consist in fitting sundry equations on to curves. . . . . It is quite true that if a curve differentiates into a straight line an equation of a certain form must represent that curve" (Journ. C. S. 1890, p. 122). It is unfortunate that Mr. Pickering has used well-known words and symbols with entirely new meanings. The operation of differentiation as usually understood cannot be applied to a curve, but only to the equation of which the curve is the graph. The differentials he uses are not infinitesimal but considerable (finite) differences.

What Mr. Pickering does, seems to be, to plot the experimental results and draw a smooth curve through them; to measure first differences (except in the case of densities), plot them out and draw a smoothed curve through them, measure second differences, plot them out and find them represented by a series of straight lines. If this account of the method be correct there seem to be five chances of personal error needlessly introduced, while the smoothing process, if accurately performed, ought to get rid of those slight changes in first differences which in the second differences mark changes of curvature, and therefore by hypothesis changes of hydration. The method seems to be distinct from that of Mendeléeff, though stated by Mr. Pickering to be the same.

(2) Mr. Pickering further says:—"The method would give absolutely true results only if these differences were infinitely small; if they are reduced too much, generally below 1 per cent., the experimental errors attain such relatively large proportions that the results are useless." "When a second differentiation has to be performed it is hardly possible to apply it to the experimental values themselves, as the quantities dealt with would be about the same magnitude as the experimental errors themselves" (Journ. C. S. 1890, p. 67).

These sentences seem to carry with them the condemnation of the method. If the original results are not sufficiently accurate to warrant second differences, no manipulation of a steel lath, however skilful, can make them so. Hence in the case of experiments of such extreme delicacy it seems preferable to throw over the graphical method altogether, and tabulate the finite differences as suggested under empirical methods, more especially as they afford a test of how far it is safe to carry the reduced results. The following Table is thus obtained from Mr. Pickering's results. The frequent changes of value and sign in the third differences shows that the accuracy of the experiments does not warrant us in carrying the equation to the third power of the variable. Let us then attempt to find an equation of the second degree which adequately expresses Mr. Pickering's results :—

$$c = \delta^2 u = \cdot 0000471 \text{ nearly.}$$

$$b = \delta u - \overline{x_2 + x_1}\ \delta^2 u = \cdot 01071616 - 119\cdot 9711 \times \cdot 0000471$$
$$= \cdot 00506552.$$

$$a = u - bx - cx^2 = 1\cdot 4809752 - \cdot 00506552 \times 58\cdot 992484$$
$$- \cdot 0000471 \times 3512\cdot 6.$$
$$a = 1\cdot 016704.$$

$$\therefore u_x = 1\cdot 016704 + \cdot 00506552x + \cdot 0000471x^2;$$

from which the column of calculated values has been obtained. Since no one of the calculated results differs from that observed by so much as one part in five thousand, the equation probably expresses the results well within the limits of experimental error, and with far greater accuracy than could be attained by even the most careful drawing. Probably with greater arithmetical labour the calculated and observed results could be brought even more closely together. But the fact of this continuous curve running so well among the experimental results seems to throw very grave suspicion on the definite hydrate $H_2SO_4\ 3\cdot 92H_2O$ containing 57 per cent. of real acid which Mr. Pickering obtains from these experiments.

The whole question then seems to depend upon the extent to which we can *safely* rely upon the experimental results. If the limits of accuracy are 1/5000, the results can be expressed by a (smooth) single curve represented by an equation of the second degree ; and this equation when differentiated gives an equation of the first degree, which can be expressed by a straight line.

x.	x_2-x_1.	x_3-x_1.	x_4-x_1.	x^2.	u at 28·064°.	δu.	$\delta^2 u$.	$\delta^3 u$.	u calc.	u cal. − u obs.
50·06998	1·95683	3·93144	5·93916	2507	1·388553	·0097842	·00004675	·00000274	1·388414	−·000139
52·02681	1·97461	3·98233	5·82908	2707	1·407699	·0099680	6303	− 0209	1·407737	+·000038
54·00142	2·00772	3·85447	5·96910	2916	1·427382	·0102190	5086	+ 0519	1·427284	−·000098
56·00914	1·84675	3·96138	5·90291	3137	1·447899	·0104150	8180	− 1366	1·448173	+·000274
57·85589	2·11463	4·05616	6·18946	3346	1·467133	·0107390	0113	+ 1580	1·467432	+·000299
59·97052	1·94153	4·07483	6·05465	3596	1·489842	·0107436	9892	− 1251	1·489879	+·000037
61·91205	2·13330	4·11312	6·09646	3832	1·510701	·0111466	2318	+ 0231	1·510438	−·000263
64·04535	1·97982	3·96316	5·88604	4101	1·534480	·0112419	3719	− 0085	1·534322	−·000158
66·02517	1·98334	3·90622	5·99715	4359	1·556737	·0113893	3218	+ 0059	1·556480	−·000257
68·00851	1·92288	4·01381	5·97792	4625	1·579326	·0115150	3575	− 0662	1·579048	−·000278
69·93139	2·09093	4·05504			1·601468	·0116585	− 0382			
72·02232	1·96411				1·625844	·0116430				
73·98643					1·648712				1·649309	+·000597
58·99248 4				3512 6	1·4809752	·01071616	·00004707 9			

In conclusion, it need hardly be pointed out that, even if these criticisms be admitted, they do not impugn the *great* accuracy of Mr. Pickering's results, but only the *extreme* accuracy necessary for his purpose ; further they do not of course disprove the hydrate theory, but only reduce it, so far as they go, to the condition known in Scottish law as not proven.

LI. *Note on a peculiar Determinant of the Sixth Order.* *By* Thomas Muir, *LL.D.**

In the Philosophical Magazine for March 1856 (vol. xi. pp. 378, 379) Professor Cayley gave, as a bye-result of a process of elimination, the curious identity

$$\begin{vmatrix} . & C & B & -2A' & . & . \\ C & . & A & . & -2B' & . \\ B & A & . & . & . & -2C' \\ A' & . & . & A & -C' & -B' \\ . & B' & . & -C' & B & -A' \\ . & . & C' & -B' & -A' & C \end{vmatrix} = -2 \begin{vmatrix} A & C' & B' \\ C' & B & A' \\ B' & A' & C \end{vmatrix}^2,$$

or, as he shortly writes it,

$$\square = -2K^2,$$

concluding his note with the remark, "It would be interesting to show *à priori* that $\square$ contains K^2 as a factor." The appositeness of the remark is not a little enhanced when it is recalled that Sylvester, who was the first† to light upon $\square$, made it out to be equal to

$$ABC(ABC - AB'^2 - BC'^2 - CA'^2 + 2A'B'C'),$$

i. e.

$$ABC \begin{vmatrix} A & A' & C' \\ A' & B & B' \\ C' & B' & C \end{vmatrix}.$$

The object of the present short note is to supply Professor Cayley's desideratum.

* Communicated by the Author.

† See his ingenious paper, "Examples of the Dialytic Method of Elimination as applied to Ternary Systems of Equations," Cambridge Math. Journ. ii. (1841) pp. 232-236.

Multiplying

$$\begin{vmatrix} -\frac{1}{2}AC' & -\frac{1}{2}BC' & \frac{1}{2}CC' & . & . & AB \\ -\frac{1}{2}AB' & \frac{1}{2}BB' & -\frac{1}{2}CB' & . & CA & . \\ \frac{1}{2}AA' & -\frac{1}{2}BA' & -\frac{1}{2}CA' & BC & . & . \\ . & . & 1 & . & . & . \\ . & 1 & . & . & . & . \\ 1 & . & . & . & . & . \end{vmatrix}$$

by $\square$ we obtain

$$\begin{vmatrix} . & . & . & A(A'C'-BB') & B(B'C'-AA') & C(AB-C'^2) \\ . & . & . & A(A'B'-CC') & B(AC-B'^2) & C(B'C'-AA') \\ . & . & . & A(BC-A'^2) & B(A'B'-CC') & C(A'C'-BB') \\ B & A & . & . & . & -2C' \\ C & . & A & . & -2B' & . \\ . & C & B & -2A' & . & . \end{vmatrix},$$

so that we have at once the identity

$$-A^2B^2C^2\square = -2ABC\,.\,ABC \begin{vmatrix} A'C'-BB' & B'C'-AA' & AB-C'^2 \\ A'B'-CC' & AC-B'^2 & B'C'-AA' \\ BC-A'^2 & A'B'-CC' & A'C'-BB' \end{vmatrix}.$$

But the determinant on the right here is such that if we alter the signs of the elements in its first row, third row, and second column, it becomes the adjugate of

$$\begin{vmatrix} B' & A' & C \\ C' & B & A' \\ A & C' & B' \end{vmatrix},$$

and consequently is equal to $-K^2$. All that therefore remains to be done is division by $-A^2B^2C^2$.

Bothwell, Glasgow,
April 7, 1891.

LII. *On the Variation of Surface-Tension with Temperature.* *By* Prof. A. L. Selby, *M.A., University College, Cardiff.**

MENDELEJEFF speaks of an ideal liquid as characterized by two conditions :—

(1) $V_t = V_0/(1-kt)$, V_t being the specific volume at $t°$ C.

(2) $T_t = T_0(1-at)$, T_t being the surface-tension at $t°$ C.

* Communicated by the Physical Society: read March 20, 1891.

I believe that the following proof shows that all liquids satisfy Mendelejeff's second condition.

Let unit mass of liquid have a constant volume, but variable surface S, and temperature t.

In a small change of the variables, the heat absorbed is

$$d\mathrm{H} = k dt + l d\mathrm{S},$$

k being the specific heat at constant volume, l the latent heat of extension.

The external work done on the film is

$$d\mathrm{W} = \mathrm{T} d\mathrm{S}.$$

Therefore the gain of intrinsic energy is

$$d\mathrm{H} + d\mathrm{W} = k dt + (l + \mathrm{T}) d\mathrm{S}.$$

This is a perfect differential.

Therefore

$$\frac{dk}{d\mathrm{S}} = \frac{d(l+\mathrm{T})}{dt}.$$

Also $\frac{d\mathrm{H}}{t}$ is a perfect differential.

Therefore

$$\frac{d}{d\mathrm{S}}\frac{k}{t} = \frac{d}{dt}\frac{l}{t}.$$

Therefore

$$\frac{1}{t}\frac{dk}{d\mathrm{S}} = \frac{1}{t}\frac{dl}{dt} - \frac{l}{t^2}.$$

Therefore

$$\frac{d\mathrm{T}}{dt} = -\frac{l}{t}.$$

And

$$\frac{d^2\mathrm{T}}{dt^2} = -\frac{1}{t}\frac{dl}{dt} + \frac{l}{t^2} = \frac{1}{t}\frac{dk}{d\mathrm{S}}.$$

Now k does not depend on the surface unless the film is very thin.

Therefore

$$\frac{d^2\mathrm{T}}{dt^2} = 0.$$

And

$$\mathrm{T} = c - bt,$$

where c and b may be functions of the specific volume.

That b does not depend on the specific volume may be shown as follows.

Let the liquid be maintained at constant temperature, and have a volume v and surface S; and let L be the latent heat of dilatation at constant surface.

Put the liquid through a cycle consisting of two isometries v, $v+dv$, and two lines of constant surface S, S$+d$S.

Since the cycle is reversible and the temperature is constant, the heat absorbed is zero.

Therefore

$$\frac{dl}{dv}=\frac{d\mathrm{L}}{d\mathrm{S}}=0.$$

Therefore l is independent of v, and so is b since $l=bt$.

Thus the latent heat of extension is proportional to the absolute temperature. This agrees with a hypothesis of Clausius (Phil. Mag. 1862, vol. xxiv.).

It has been shown that T can be expressed in the form

$$f(v)-bt.$$

We shall show that it can also be written $\phi(p)-bt$.

For let the pressure of the liquid remain constant while the surface, volume, and temperature vary.

Then

$$d\mathrm{H}=\mathrm{K}dt+ld\mathrm{S},$$

K being the specific heat at constant pressure and l having the same meaning as before, for the latent heat of extension at constant temperature and volume is also the latent heat of extension at constant pressure (and temperature).

The external work done on the liquid is

$$d\mathrm{W}=\mathrm{T}d\mathrm{S}-p\frac{dv}{dt}dt,$$

p being regarded as constant in forming $\frac{dv}{dt}$.

Therefore,

$$d\mathrm{H}+d\mathrm{W}=\left(\mathrm{K}-p\frac{dv}{dt}\right)dt+(l+\mathrm{T})d\mathrm{S}.$$

Since this is a perfect differential,

$$\frac{d}{dt}(l+\mathrm{T})=\frac{d}{d\mathrm{S}}\left(\mathrm{K}-p\frac{dv}{dt}\right)=0, \text{ except for a very thin film.}$$

Now $l=bt.$

Therefore $\mathrm{T}=\phi(p)-bt.$

But the two expressions $\phi(\rho)-bt$ and $f(v)-bt$ can only be identical at all temperatures if $f(v)$ and $\phi(\rho)$ are both equal to a constant c.

Therefore

$$T=c-bt,$$

where c and b are constant.

It appears then that the surface-tension of a liquid is independent of the pressure and depends only on the temperature, unless the film is very thin.

The critical temperature is c/b, and can be found by determining the surface-tension at two very different temperatures.

LIII. *On some New Methods of Investigating the Points of Recalescence in Steel and Iron.* *By* FREDERICK J. SMITH, *Trinity College, Oxford**.

IT was discovered by Mr. Gore, in 1869, that when an iron wire was heated to redness, and then allowed to cool, a momentary elongation of the wire took place immediately after it began to cool. The phenomenon was made evident by means of a suitably arranged pointer (Proc. R. S. 1869). The phenomenon was next investigated by Prof. Barrett, and it was shown by him to be due to a reheating of the wire: the phenomenon has been called by him Recalescence (Phil. Mag. 1873). Recently M. Osmond has observed that there appear to be two points at which on cooling the phenomena occur (*Compt. Rendus*, 1890).

I have not mentioned other work which has been done on recalescence, as it would have no immediate bearing on the subject of this communication. I have been led to make some experiments on recalescence, with a view to discover what part it may play in the destruction of certain engineering structures, such as heavy coiled guns, and those parts of boilers which are exposed to the effects of fire.

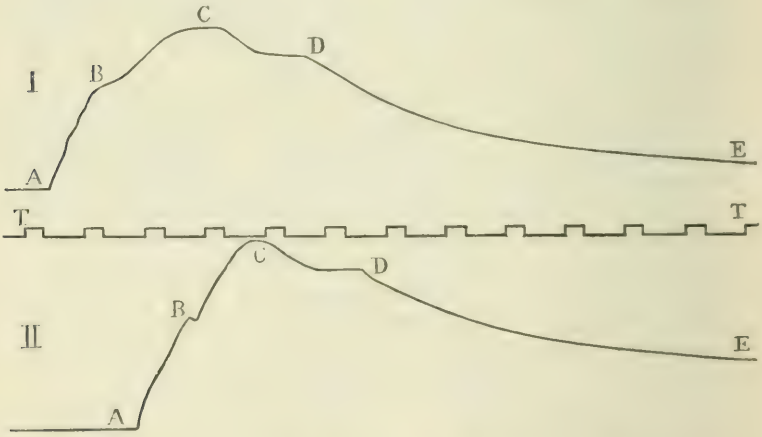
Up to the present time, observations have been made on the changes of temperature apart from the lengthening and shortening of the steel and iron under examination. I wished, if possible, to discover the time-connexion which exists between the change of form and the change of temperature. Several methods of experimentation were tried, and finally the following ones were found to give satisfactory results.

The upper end of the steel wire to be tested was fixed vertically; the lower end was attached to a long light lever of aluminium, so arranged that a small change of length of

* Communicated by the Author.

the wire caused a large movement of the end of the lever, which traced a line on the smoked surface of paper rotating on an ordinary physiological chronograph cylinder. A thermo-couple made up of two wires, one of platinum, the other of platinum alloyed with 10 per cent. of rhodium, was twisted round the wire where it was heated; the thermo-couple was in circuit with a Depretz D'Arsonval galvanometer. By means of this combination the temperatures at which the changes of length of the wire took place were read. The movements of the beam of light reflected from the galvanometer were recorded on a moving photographic film.

The outcome of the experiments made with this arrangement was that the changes of form of the metal under examination took place at the times of change of temperature, so that a curve so traced on the smoked paper can be used as an index of the changes of form and the changes of temperature. While an experiment was going on, electrically controlled styli marked the time on the smoked paper and on the photographic record second by second.



Two copies of curves traced by this method are given, numbered I and II. They show that on heating the wire it expands up to a point B, and then stops, although the heat is supplied to the wire at a uniform rate, it next expands up to C; heat then being taken off, it contracts to D, where for a short time it ceases to contract, it then contracts to E. The time is marked on the zigzag line T T every two seconds. So far two critical points are made evident. The wires used in tracing the curves I and II were differently loaded; this

caused the point I to be differently placed in the two experiments. The wire in II carried the greater load. If the wires are not loaded, the critical points are found to be at the same height of ordinate.

While I was working on the subject, it seemed probable that the curious changes which took place in a wire when heated and cooled might possibly be accompanied by some sounds at the critical points. By means of a piece of apparatus of simple construction I found this to be the case. The apparatus was constructed thus:—A disk of mica 5 centim. in diameter was fitted, like a telephone disk, into a circular recess, turned out of a piece of wood. The disk was fixed at right angles to a table. The steel wire under examination was attached at one end to the centre of the disk, at the other to a vertical post. The length of the wires tried varied between 5 centim. and 20 centim.; the diameters of the wires used were about 0·5 millim. to 1·0 millim. The front of the recess into which the mica disk was fitted was furnished with two tubes, by means of which any sounds from the disk might be conducted to the ears.

After the tubes were fixed to the ears, a flame was applied to the wire, usually the tip of a small Bunsen burner. On heating the wire a certain temperature was reached at which a sharp crackling sound was heard. As the temperature was increased this ceased; then, on removing the flame, at the same temperature at which the first sound was heard, a second similar sound occurred. This took place at the point of recalescence. As the wire cooled this ceased, and then, when a temperature of about 490° C. was reached, a very sharp sound was emitted. This third sound is, I believe, of interest, as it appears to take place at the second critical point observed by M. Osmond. During this sound experiment, the temperature was observed by means of the thermo-couple and galvanometer. When the disk was furnished with a hollow cone, as used in connexion with the phonograph, a person could hear the effect at a distance of ten feet from the apparatus. The first two sounds are of short duration, and might easily be missed, if not carefully listened for; but the third sound is clear and definite. The wire used in these experiments was steel pianoforte wire, annealed and straightened. I was unable to get the effect when a wide flame was used, but with a flame about 1 centim. wide the curious effect can be produced fifty times following from the same wire. The last experiment was also arranged so that the steel wire when heated should be in a strong magnetic field, produced by a helix through the axis of which the steel wire passed.

Repeated trials showed that the sounds produced were in no way altered by the fact of the wire being in the magnetic field.

The former method of the trace on smoked paper has been used by me in the Millard Laboratory for getting traces of the expansion and contraction of bars of different metals up to 2 centim. diameter, heated over a part of their length in a gas furnace.

San Remo, March 28, 1891.

LIV. *Notices respecting New Books.*

A Dictionary of Metric and other useful Measures. By Latimer Clark, *F.R.S.* (London: E. & F. N. Spon.)

ONE of the most marked characteristics of the progress of Science is to be found in the gradual decay of the old rule of thumb methods of calculation formerly in use among practical men. The development of scientific methods in all branches of commerce necessitates not only a greater, but also a more accurate, knowledge of the relations between the units of measurement in various trades and in different countries. Also the daily increase in the number of practical applications of electricity has caused attention to be directed to its units of measurement; and it is to be hoped that the simplicity of these units will lead finally to their universal adoption.

In the volume before us Mr. Clark has arranged all the principal units of measurement in alphabetical order and given definitions of each; he has also given multiplying factors for the conversion from one system of units to another. For those who prefer logarithmic computations the logarithms of these factors are given with five-figure accuracy, and a table of five-figure logarithms is also added at the end of the book. The work is very complete and has been brought quite up to date, the mass of a cubic inch of water for example being given as 252·286 grains as legalized by the Board of Trade in 1890, thus displacing the previous number, viz., 252·458 grains. The units given include almost all in commercial use, and range from the law-writer's "folio" to the unit of self-induction. The apothecaries' weights and measures have not been forgotten, and should prove useful to many a photographer. The alphabetical arrangement is very convenient, and any required unit can be found at once. The book is, moreover, for a work of this kind, singularly free from errors. Its figures are printed in a good, bold type, very unlike that of the familiar engineers' and electricians' pocket-books, but none the less commendable.

James L. Howard.

Index of Spectra. By W. Marshall Watts, *D.Sc., F.I.C.* (Manchester: Abel Heywood & Son.)

This book appears as a revised and greatly enlarged edition of the original work with the same title, which was published in

1872. Since that time (in 1884) a Committee of the British Association, of which the author was Secretary, has collected all the results of various observers relating to the spectra of the elements, and has printed them in the Reports of the Association. In the present volume all these results are reprinted together with others published since the Committee finished its work. It does not, however, contain the most recent measurements made with the large diffraction-gratings at the Johns Hopkins University by Prof. Rowland and his colleagues. Indeed the numbers given in the tables were all obtained from prismatic spectra, and corrected, of course, for the irregularities in the dispersion of the prism. In the preface Dr. Watts gives a table of corrections for reducing Ångström's and Cornu's measurements to the standard of Rowland's map. This is presumably the map issued in 1888, which, if we remember rightly, Prof. Rowland stated to be in some respects erroneous; at any rate not so accurate as the more recent one (1889). The author has introduced a new feature into this Index in the shape of a column of oscillation frequencies, these being the reciprocals of the wave-lengths. This column ought to be very useful in ascertaining any harmonic relations which may exist between the various lines in the spectrum. The Index contains a very large amount of information concentrated into a small compass. By its means it should be possible to identify with comparative ease any unknown element which happens to be under examination. We are glad to learn that Dr. Watts contemplates issuing an Atlas of Spectra as a companion to the book before us. The Atlas is to be constructed so that the intervals between the lines will be proportional to their differences of oscillation frequency. This will differ considerably from Rowland's map, where the distance between two lines is proportional to their difference in wave-length. Dr. Watts's map should show at a glance what relations, if any, exist between the various lines given by any element. J. L. H.

The Phonopore and the Simplex Phonopore Telegraph. By C. Langdon-Davies. (London: Kegan Paul, Trench, Trübner, & Co.)

If two insulated wires be wound side by side on a bobbin so that a current passed through one acts inductively on the other, it is well known that, if one end of the secondary coil be insulated and the other joined up to a telephone and a galvanometer whose second terminal is likewise insulated, whenever a current is made or broken in the primary coil the telephone of the secondary coil gives a click, but the galvanometer shows no effect. By periodically repeating the making and breaking of the primary current, we can produce a musical note in the telephone, but the galvanometer is still undisturbed. The author has made use of this fact in the phonopore, which consists of two coils, as described above, and which he proposes to apply to a new system of duplex telegraphy.

The one set of messages is to be transmitted and received by an ordinary Morse installation working with constant currents. For the other set of messages the phonopore is used, its primary coil being connected simply to a spring by which its current is automatically made or broken periodically, and to a key for sending messages. The secondary coil has one end insulated and the other connected to the line. The second set of messages is therefore a series of breaks in an otherwise periodically made and broken current. The receiver for these messages is somewhat complicated and very ingenious. It possesses a spring whose rate of vibration coincides with that of the harmonically interrupted current, and it is therefore not affected by irregular disturbances. The system seems quite good in principle, and is an ingenious and extremely interesting attempt to put the idea of Elisha Gray's harmonic telegraph into a workable form. The author points out that his telegraph can be added to any previously existing installation, and he has made crucial experiments on several lines both in England and abroad. The reports given by eye-witnesses of these experiments are incorporated in the book before us, and they seem to promise well for the ultimate success of the system. J. L. H.

Reduction Tables for Readings by the Gauss-Poggendorff Mirror Method. Czermak. (Berlin: Julius Springer.)

Whenever a mirror-and-scale method is used for the measurement of small angles some trouble is experienced in reducing the observations, because the scale-readings are proportional to the tangent of twice the angle of deflexion, whereas we generally require either the angle of deflexion itself, its tangent, or else, as in the ballistic galvanometer, the sine of half of it. The object of these tables is to enable an observer to write down at once, knowing the distance between his mirror and scale and the scale-reading, a number proportional to the quantity he wishes to measure in any experiment. There are four tables given in order to find the angle of deflexion in degrees or in circular measure, the tangent of the angle of deflexion and the sine of half of it, respectively. The method of reduction and the process by which it is arrived at are described in English, French, and German, at the beginning of the book. The tables will prove useful to those who are in the habit of making series of observations with a mirror and scale, though the method is far more frequently resorted to on the Continent than in England, null methods being here in more general use. J. L. H.

An Introduction to Dynamics, including Kinematics, Kinetics, and Statics, with numerous examples. By C. V. Burton, *D.Sc.* (London: Longmans. Pp. xiii + 392.)

The first seven chapters (with the exception of chapter iii. which treats of the trigonometry of one angle, for the benefit of readers

who have no previous knowledge of this subject) are devoted to Kinematics, up to and inclusive of Projectiles. Chapters x. to xiii. are mainly occupied with Statics: in chapter xiv. several problems in Statics are discussed: the remaining chapters (viii., ix., xv. to xvii.) treat of Kinetics, and the last chapter (xviii.) is taken up with the dimensions of Units. In the main body of the work are numerous examples, some of which are very fully and carefully worked out. At the end are a number of additional exercises, arranged under the subjects of the previous chapters; these have, in the main, been taken from London University examination papers. To all the Examples answers are given. Original treatment is not to be looked for in a work of this character, which is written for Students preparing for the above-named and similar examinations. But what we have found is that great pains have been taken in clearing up difficulties which young students meet with in this subject; and this we state though here and there are small oversights, as on p. 21 and one or two other places. These can easily be removed in a subsequent edition. Some parts, notably the earlier chapters, and bits here and there in later chapters, are very well done; and in the other weaker parts Dr. Burton sins, if he does sin, with the majority of elementary text-book compilers.

LV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 288.]

February 25, 1891.—Dr. A. Geikie, F.R.S., President, in the Chair.

THE following communications were read:—

1. "A Contribution to the Geology of the Southern Transvaal." By W. H. Penning, Esq., F.G.S.

The following table shows the author's classification of the sedimentary rocks of this region, as compared with those of Messrs. Dunn and Stow and Prof. Rupert Jones:—

Dunn. (Map, 1887).		Stow.	T. R. Jones.		Penning.		
Coal-measures: *Upper Karoo* (formerly Stormberg Beds, above Upper Karoo).	Carboniferous to Triassic.	*Upper Karoo.*	*Lower Karoo.*	Triassic Formation.	*High Veldt Beds.*	Oolitic.	
Kimberley Shales: *Lower Karoo* (formerly Upper Karoo).		.....			*Kimberley Beds.*		
Lydenburg Beds.	Silurian.				*Klip River Series.*	Devonian.	
					Witwatersrand Series.		Magaliesberg Formation.
Namaqualand Schists.					*De Kaap-Valley Beds.*	Silurian.	

The De Kaap-Valley Beds consist of schists, shales, cherts, and quartzites, with some conglomerates, chloritic, and steatitic beds of great thickness, faulted, according to the author, against the granite. They contain a few obscure corals, and are provisionally referred to the Silurian.

The Witwatersrand Series consists chiefly of sandstones, shales, cherts, and quartzites, having an estimated thickness of 18,000 feet, possibly formed in a hollow of the granite, and perhaps of marine formation.

The Klip-River Series is formed of shales, flagstones, cherts, and quartzites, with numerous interstratified traps, and is at least 18,000 feet thick. Near its base is the "Black Reef" and a chalcedonite like that described by the author in connexion with the Lydenberg district, which confirms his opinion that this area is formed of part of the Megaliesberg formation. The base of the series is generally conformable to the underlying rocks. The whole of the lower half of the Megaliesberg formation is let down against the north side of the granite S. of Pretoria.

The author divides the formation which he described in 1884 under the heading of High-Level Coalfields of South Africa into the Kimberley Beds and the High Veldt Beds. The former thin out eastward, and are overlapped by the latter, the estimated thickness of which is 2300 feet. A volcanic rock overlies the Coal-formation. Near the base of the formation is a bed of loose, calcareous, sandy clay enclosing many waterworn pebbles, some of large size, derived from the quartzites and "Bankets" of the underlying formation. The author is convinced that the region was under glacial influences at some time during the long period which intervened between the deposition of the Megaliesberg formation and of the coal-bearing rocks of the High Veldt, which latter, he maintains, are certainly Oolitic; the latter contain *Glossopteris* (?) and fishes, which he considers to be nearly allied to *Lepidotus valdensis*, the latter being from the Free State.

The High-Veldt rocks are of fluviatile origin, and there appears to have been continuity of fluviatile denudation from the close of the Oolitic period until now.

2. "On the Lower Limit of the Cambrian Series in N.W. Caernarvonshire." By Miss Catherine A. Raisin, B.Sc.

In this paper the author examines the questions, whether the Bangor beds should be included in the Cambrian Series, and how the strata associated with the southern felstone should be classed. The lithological character of the rocks overlying the conglomerate at Bangor is shown to be of little classificatory value, but the apparent discordance between its strike and that of the beds beneath suggests the inclusion of the latter in the Pre-cambrian series, as maintained by Prof. Hughes and Prof. Bonney.

The age of the northern beds must depend, however, to a great extent upon the classification adopted for the Llyn Padarn rocks.

It has recently been proposed to regard the felstone of this district as a lava-flow of Mid-Cambrian age, and the beds to the north as lower strata included in the same great series. The author points out as objections to this view:—(1) the enormous thickness of beds, which in that case must be cut out by the supposed Arenig unconformity at Caernarvon; (2) the difficulty of assigning two felsite masses lithologically similar to two distinct periods; and (3) the occurrence of conglomerates similar to those which are elsewhere admitted to be basal Cambrian. But in addition to these minor difficulties, the theory of a Mid-Cambrian age for the above-named lava is shown to be without foundation. It was supposed that in the Bryn Efail quarry the slaty rocks of the district immediately to the north could be seen in contact with, and altered by, this lava. The author shows that no slate occurs in the quarry, a diabase having apparently been mistaken for it, and that there is no grit in the section which would afford any support to the new theory. The author concludes that the Llyn Padarn felsite is probably, as classed by Dr. Hicks and Prof. Bonney, of pre-Cambrian age. As regards the country to the north, the argument for the arrangement was based mainly on the interpretation of the Bryn Efail rocks; but as this is seen to be erroneous, the section founded on it does not appear preferable in any way to that published by the Geological Survey.

LVI. *Intelligence and Miscellaneous Articles.*

SOME REMARKS ON THE KINETIC THEORY OF GASES.

BY S. TOLVER PRESTON.

THE theorem that the velocities of the molecules of a gas vary "between zero and infinity" (between zero and a velocity indefinitely great) would seem to give the idea that the velocities are enormously great sometimes.

But it would appear that there are distinct physical conditions tending to limit the velocities of the molecules of a gas (*i. e.* the velocities capable of being acquired in the accidents of collision). First, there is the friction of the molecules in their passage through the æther. This must be considerable at high velocities, since meteoric dust is measurably retarded from this cause; and the relative friction or resistance to passage increases as the size of the body diminishes. So that probably by the known small size of molecules, the friction must be very great. Second, the resistance to passage is augmented from the fact that the molecule is in vibration (or some analogous motion about its centre of gravity) in the æther. The molecule is like a rough body then, stirring up the æther during its translatory motion, which must greatly augment the resistance to passage. That there is friction in the æther by the passage of molecules is also confirmed, as it seems, by the fact that waves of heat and light contain energy. For how

should a vibrating molecule impart energy to the æther without friction or resistance? The resistance is in fact a measure of the energy imparted. It appears a question whether, if the amplitude of the vibration (or motion which stirs up the æther) of molecules were known, the friction or resistance could not be calculated therefrom. For we know the number of vibrations accurately by the spectroscope, and the energy imparted to the æther (or contained in the waves), by the thermopile. To deduce the resistance to passage represented by the act of vibrating or swinging, we only appear to require the amplitude of vibration then. Perhaps a limiting value for this could be approximately arrived at.

Another cause tending to reduce the velocity of translatory motion possible to the molecules of gases in the accidents of collision, consists obviously in the fact that the internal motion of the molecule (vibration, rotation, &c.) is proportional to the translatory velocity. So if a molecule attained an excessive translatory velocity, it would acquire an excessive vibration. This vibration would soon dissipate the energy in the æther in the form of waves of heat; and at the next succeeding collisions, the molecule would acquire a relatively slower translatory motion, as it could not retain the necessary vibratory motion (internal motion) which is the essential accompaniment of a very high translatory velocity. So therefore, from all these causes, the speeds capable of being acquired by the molecules of gases in the accidents of their encounters, are probably moderate; and far less perhaps than might be inferred from the theorem that the velocities vary between zero and a velocity indefinitely great.

Refering to a letter received from the late Prof. Clerk Maxwell, I find that—"The number of molecules whose velocity is more than five times the mean velocity is an exceedingly small fraction of the whole number, less than one millionth. But if there were 10^{20} molecules, many millions of these would have velocities greater than five times the mean, and yet this would produce no appreciable effect on the whole mass."

It seems, then, from the above that the number of molecules attaining high speeds is relatively rare. But it appears none the less worth noting distinctly that an indefinitely great velocity would mean a velocity indefinitely greater than the speed of light even. Suppose a few molecules to attain extreme stellar velocities of say 200 miles per second; it is evident that the friction in the æther (appreciable in the case of meteoric dust) would commence to tell in reducing the velocity. And as for a molecule supposed to acquire the speed of light itself, the molecule would (in traversing the æther) resemble much a cannon ball moving through the air at the normal speed of the air-molecules themselves—about 1600 feet per second—where the resistance to passage is very considerable, so it seems that there are in practice physical conditions limiting the velocities attainable by the molecules of gases; the resistance to passage augmenting more than in proportion to the velocity.

It is not at all as if those molecules were moving in empty space. A molecule, if assumed to acquire an infinite velocity, would certainly have to be assumed to possess an infinite energy. It may be questioned whether even the total energy of translatory motion of the stars in the collective universe is infinite in sum; if not, then a single molecule with a supposed infinite velocity would require to have a greater total energy than this. The expression "infinite velocity" apparently only comes into the mathematical calculations applicable to a gas, supposed infinite in extent. But in these calculations it seems tacitly to be supposed that the molecules are moving in empty space, which is, however, not a fact. On the contrary*, the molecules move in a resisting substance whose obstruction to motion increases in a high ratio with the velocity of the bodies which traverse the resisting substance.

Hamburg, March 1891.

THE LIGHTNING DISCHARGE. BY S. TOLVER PRESTON.

Prof. Colladon has stated from personal observation ('Nature,' July 1, 1880) that trees struck by lightning give indication of a

* The late Prof. Clerk Maxwell arrived at some data as to the size &c. of molecules. If we assume a hydrogen molecule to vibrate through an amplitude (say) two thirds of its diameter at a certain temperature, we can obviously get the total distance traversed through the æther in one second by the molecule through its vibrations, *i. e.* the total distance the molecule would have traversed if, instead of oscillating, it had moved through the same total distance per second in a straight line. I find this distance to be about ninety miles, *i. e.* the molecule vibrates at the rate of ninety miles per second, by the above assumed amplitude of vibration in terms of dimensions of molecule (which seems quite possible). According to Maxwell, two million hydrogen molecules placed in a row would occupy a millimetre. Hence it appears practicable that molecules can vibrate at a *greater* rate than a planetary velocity, which may seem surprising to some, considering how small the dimensions of molecules are (and therefore their amplitudes of movement). The velocity of the earth in its orbit, for instance, is eighteen miles per second, as is known. The above comparatively high estimate for vibratory velocity of molecules (ninety miles per second, only a rough estimate of course) may account rationally for the energy contained in the heat-waves of gases and other bodies, which (energy) is a measure of the friction or resistance opposed by the æther to the vibration or movement of a body in it. Calculations of this kind, although of course only approximate, may give us conceptions or ideas of the æther structure. If I had by me data as to the energy of the waves emitted by a gas (radiating power), it would obviously not be difficult to compute the static resistance opposed by the æther to the vibratory movement or swing of the molecule in it, in terms of the weight of the molecule, *i. e.* in terms of gravity. Whether we have here a swing of the molecule, a movement of rotation oscillatory in its nature, or any movement of a repeated kind, the same considerations evidently in principle apply.

radial disturbance; or the intensity of the destructive effect on leaves, branches, &c. increases radially towards an axial line, where the effect is a maximum, or explosive.

Before this observation, or in 1876, I had published two articles in 'Engineering,' (March 17 and 31, 1876), where, in regard to the lightning discharge, the above radial movement towards an axial line—which constitutes the "spark"—was suggested on theoretical grounds to be a fact; so that I may be allowed to add a few remarks on this point here, referring to the above-named articles for more detail. The idea that static electricity is a "resonance" of the æther (confirmed experimentally since by the discoveries of Prof. Hertz) is speculatively advanced in these articles, and it was mentioned in a work, 'Physics of the Ether' (E. and F. N. Spon, London), published by me in 1875. I cannot do better than quote the passage, as it bears on the present case: viz.:—

"It is evident that friction or any molecular disturbance whatever would naturally throw the æther within a mass of matter into vibration. The stationary vibration of a mass of æther has its analogy in the stationary vibration—'resonance'—of a mass of air, produced by friction &c. The change of '*static*' electricity into '*dynamic*' electricity, or the '*static*' state into the '*dynamic*' state, and conversely, is simply the change of *stationary* vibrations into *progressive* vibrations, the one being necessarily always capable of producing the other ('Physics of the Ether,' p. 133).

As we may sometimes arrive at initiatory ideas of the *modus operandi* of phenomena, which may usefully aid towards their final solution, no further excuse is probably needed for the considerations which follow.

The spark or lightning-flash will be found at least, I believe, to consist in the breaking, through loss of equilibrium, of a "resonance" column of æther (which vibrated radially about a central rarefied* axis, and partly longitudinally), the loss of equilibrium being followed by the resolution of stationary waves into progressive waves, with the movement of these waves radially (in the main) from all sides towards a central or axial line, where they rebound with explosive effect. In this way energy is drawn from a wide radial extent or volume of the æther and concentrated suddenly on a single line (the axis), which produces a violent condensation of the æther along this line, instantly followed by an explosive rebound, as the æther recovers its equilibrium, with the velocity of light. If the trunk of a tree, for example, happens to be situated in this æther rarefaction (where the "attraction" is a maximum just before the flash is observed), then, since the æther is known to penetrate the substance of the tree freely, it becomes clear enough, as a mechanical fact, that on such a violent conden-

* The rarefied axis constitutes a point of stability to vibrate about, just as the rarefaction in a column of air (in a pipe) open at both ends constitutes a point of stability for the resonance of the air-column.

sation of the æther occurring inside the trunk of the tree and exploding (laterally all round) outwards with the velocity of light, the trunk is shivered into fibres. In fact this is the exact effect that might be expected from the above conditions. The æther may of course in its normal state exercise very great pressure (many tons on the square inch).

The passage from 'Nature' describing the observation of Prof. Colladon may be appended here; viz.:—

"The Professor contends that it (the lightning) falls in a shower, not in a particular flash, and that it *runs along branches of trees until it is all gathered in the trunk*, which it twists or tears open in its effort to reach the ground. In the instance in question, the trunk of the cherry-tree is as completely shivered as if it had been exploded by a charge of dynamite" (p. 204).

The italicised passage tends to show a radial * (wave) movement of matter from all sides simultaneously, or is consistent therewith. It seems to be popularly suposed that the movement of matter is propulsively *along the line* of flash (not sideways or radially towards where the flash shows itself); this is why, no doubt, according to the popular motion, it becomes utterly impossible to form a mechanical idea as to how such destructive effects are produced by lightning.

The above suggestion makes no pretention to exactness or precision as to the *modus operandi* of a lightning discharge. There are reasons, however, for believing that the idea is true on certain broad or fundamental points (on account of its apparent mechanical fitness); and the idea may invite others to reflect on the subject, which can conduce to progress.

As regards the "attraction" produced by vibration, the phenomenon of "resonance" &c., the writer may mention briefly some experiments made by himself some seven years ago. The object was to augment the effects of attraction by trying the influence of larger vibrating bodies than had hitherto been done. For this purpose, tuning-forks weighing some four to five pounds each were taken. When such a fork was thrown into vibration by a blow, it was found possible to suspend floating in the air below the prong, pieces of cardboard, upwards of 4 inches long, $\frac{3}{4}$ inch wide, and about $\frac{1}{10}$ inch thick. This therefore being so distinct and palpable an instance of attraction by vibration or resonance, may have interest especially in reference to the recent experimental confirmation of the fact that static electricity (which can "attract") is also a phenomenon of "resonance."

Hamburg, Jan. 1891.

* Although the case is not strictly parallel, of course, a wave-movement of the æther sideways towards a line may be seen in the line-focus of a cylindrical lens.

ELECTRICAL OBSERVATIONS ON THE HOHER SONNBLICK. BY PROFS. ELSTER AND GEITEL.

From the results of a series of experiments and of observations on the Hoher Sonnblick at a height of 10,168 feet above the sea-level, the authors draw the following conclusions.

1. The intensity of the most refrangible rays of the sun's spectrum as measured by its discharging action on negatively electrified surfaces of amalgamated zinc, increases with the height above level ground, in such a manner that at a height of 10,168 feet it is *twice* as great as on ordinary level ground.

2. Notwithstanding this increase in the power of discharge of light, we did not succeed in establishing with certainty any new actinometrically active substances; even perfectly pure freshly fallen snow as well as dry rock taken from the ridge of the Sonnblick were not appreciably discharged by light.

3. Waterfalls can produce negative falls of potential in a valley, and even to considerable heights, 1600 feet.

It may be presumed that this remarkable phenomenon is not produced by friction, but by the influence of the normal positive fall of potential on the finer pulverulent water which detaches itself from the large masses of water. And it may perhaps be assumed that, as in a rain-cloud, the process of self-induction increases to high values the originally feeble negative charges of a layer of air-dust at the foot of the fall.

4. In July of this year (1890), on three days which were almost cloudless until 1 P.M., the normal positive fall of potential on the top of the Sonnblick was appreciably constant. The morning maximum, which in the plain and in Alpine valleys occurs with great regularity between 7 A.M. and 9 A.M., was *not* observed at a height of 10,168 feet.

5. Before the outburst of the storms which we observed on the 16th, 18th, and 20th July, the positive fall of potential, within the cloud which sent only a small quantity of rain, sunk slowly down to the value zero, at which it then remained for a long time, perhaps two to three hours, until the electrical process in the cloud definitely came to an end.

6. In storm-clouds the atmospheric electricity usually changes its sign after a discharge of lightning, as with storms in the plain.

7. St. Elmo's fire was found to constantly accompany storms; it was not found that *negative* St. Elmo's fire was more infrequent than *positive*.

8. The observation that negative St. Elmo's fire follows bluish lightning, and positive, reddish lightning, was frequently confirmed by us. The direction then of the electrical current which traverses the atmosphere in the form of lightning appears to have an influence on the colour of lightning.— *Wiener Berichte*, Nov. 1890.

ON THE ABSORPTION-SPECTRUM, AND THE COLOUR OF LIQUID OXYGEN. BY K. OLSZEWSKI.

In an earlier research the author found four absorption-bands in the spectrum of liquid oxygen corresponding to the wave-lengths 628, 577, 535, and 480. Liveing and Dewar (Phil. Mag. [5] vol. xxvi. p. 286), who observed the absorption-spectrum of gaseous oxygen in a long steel tube under high pressure, found the same four absorptions in the visible part of the spectrum, and moreover in the extreme red the bands corresponding to the Fraunhofer lines A and B, which have also been observed by Egeroff and Janssen. An apparatus recently constructed by the author for liquefying a large quantity of oxygen enabled him to repeat his former experiments, and to examine more closely the absorption-spectrum of a thicker layer of liquid oxygen in the extreme red.

The liquid oxygen was poured from the generating vessel into a thin glass tube closed at the bottom, which as a protection against external warmth was closely fitted in a set of three beakers. The thickness of the column of oxygen was 30 millim., and its height about 50 millim. The liquid oxygen maintained itself for half an hour under the pressure of the atmosphere, and at its boiling-point ($-181°{\cdot}4$) in a sufficient quantity for making the experiment, although a considerable quantity of heat was imparted to it, especially by the limelight concentrated by a condensing lens, which the author used for preparing the absorption-spectrum. A universal spectroscope by Krüss, with a Rutherford's prism, was used for investigating the absorption-spectrum. Besides the four absorptions already observed the experiments gave a fifth shadowy band, corresponding to the Fraunhofer line A, which was especially distinct when a red glass was interposed between the source of light and the slit of the spectroscope. This band appeared feebler than the three absorptions corresponding to the wave-lengths 628, 577, and 480, but stronger than the absorption 535. With this comparatively small dispersion the band A could not, of course, be resolved into lines. An absorption corresponding to Fraunhofer's line B could not also this time be observed.

Liquid oxygen has been described as a colourless body on the basis of the experiments made in 1883, in which only small quantities could be obtained. Since then the author has observed that whenever oxygen was liquefied in rather wide glass tubes, it showed in incident light in layers of about 15 millim. a bluish colour. In the experiments described above, in which for the first time a relatively large quantity of liquid oxygen was collected in a glass vessel, its bright blue colour was decidedly apparent. In order to be certain that the oxygen prepared from chlorate of potassium and manganese did not contain traces of ozone from which the colour might arise, it was carefully tested in this direction. Iodide of potassium and starch-paper was not coloured when kept

in the oxygen tested. Even when the gas was passed for some time through a solution of iodide of potassium and starch no blue colour was perceived. The oxygen used for the experiment remained for a week in the iron reservoir into which it was pumped in contact with solid potassic hydrate, by which it was completely freed from CO_2, from chlorine, and from aqueous vapour.

From these experiments there can be no doubt that oxygen in the liquid condition, and in layers of about 30 millim., has a decidedly bright blue colour. This colour of oxygen agrees very well with its absorption-spectrum. It was surprising that a colourless liquid, such as oxygen was supposed to be, had such a pronounced absorption-spectrum, in which the absorptions predominate in orange, in yellow, and in red. But this apparent contradiction has been removed by the above experiments of the author.

One word in conclusion as to the colour of the sky. There are, as it is known, so many hypotheses which attempt to explain this that the author scarcely dares to propound another. But in his opinion this phenomenon would be most readily explained by ascribing the blue colour of the sky to this constituent of the atmosphere, which has a blue colour, at any rate in the liquid state.—Wiedemann's *Annalen*, xlii. p. 663.

ON A PECULIAR CASE IN THE REFRACTION OF ORGANIC COMPOUNDS. BY R. NASINI AND T. COSTA.

The authors have found a compound formed by the simple union of two others, which, instead of having a molecular refraction double the sum of those of the components, has a far greater one. This compound is the iodide of triethylsulphine, the components being iodide and sulphide of ethyl. The constants are for the compound V, and for the mixture of both, G, 5·085 gr. of each dissolved in 100 cubic centim.

	d_4^{20}.	$^{\mu}H_{\alpha}$.	$\frac{^{\mu}H_{\alpha}^{2-1}}{d}$.	$\frac{^{\mu}H_{\alpha}^{2+2}}{(H_{\alpha}^{2-1}\mu d}$.
V	0·81761	1·36857	0·45079	0·27568
G	0·81076	1·36414	0·44926	0·27509

The sulphur has therefore a far greater atomic refraction in the compound than in the mixture. It might be supposed that this arises from the fact that the sulphur in the compound is S^{v} and in the sulphide S''; but this would not agree with the deportment of oxygen compounds in sulphur.—*Rend. R. Acc. dei Linc.* vi. pp. 259–263 (1890); *Beiblätter der Physik*, No. 2. 1891.

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[FIFTH SERIES.]

JUNE 1891.

LVII. *On the Rôle of the Cation in Voltaic Combinations; particularly those containing Chlorides of Iodine and Bromine.* By J. BROWN*.

1. SO long ago as 1851 Sir William Thomson, in referring to "galvanic arrangements adapted to allow the [chemical] combinations to take place without any evolution of heat in their own localities," defined "the intensity of an electrochemical apparatus" as "equal to the mechanical equivalent of as much of the chemical action as goes on with a current of unit strength during a unit of time"†. It has, however, been repeatedly shown that the practical application of this guarded definition is in many cases very difficult, mainly because of uncertainty as to the proportion of the total chemical action contributing to the current as distinct from other work; an uncertainty arising from want of knowledge on the following and other points:—

The exact nature of the surface of solids employed in the cell—as when metals are coated with films of oxide, carbonate or with gas-films.

Possible action of the solvent on the metals—as distinct from the dissolved electrolysable substance.

Effect of minute quantities of impurities occurring in what is considered "pure" material; such as the effect of a minute quantity of chlorine on the force of a platinum-distilled-water-magnesium cell observed by Gore ‡.

Degree of change of physical state and energy absorbed thereby.

* Communicated by the Secretaries of the Electrolysis Committee of the British Association

† Phil. Mag. ii. p. 434. ‡ Proc. Roy. Soc. xliv. p. 301.

Thermochemical data for some of the reactions involved, and some doubt as to exactness of those available and degree of their applicability to the circumstances.

Amount of some possible thermoelectric force at contacts of solids and liquids.

2. It does not therefore seem surprising that Wright and Thompson should be led to conclude from their extensive series of experiments that the electromotive force stands in no simple relationship to the chemical action or the heat evolution taking place in the cell during the passage of the current or to the heats of formation of the two substances electrolysed *.

It would have been perhaps more correct to say chemical action *assumed* to take place, and to conclude that, whether the relationship be simple or not, the chemical action is certainly not simple.

Laurie has shown † that in the case of an aluminium plate we have not to deal with the metal at the surface but partly at least with its oxide. The case of "passive" iron is also to the point.

3. Notwithstanding all this, however, there is, in any given cell, evidently a certain relationship (more or less masked by the conditions of the case) between the electromotive force and the relative chemical attractions of the positive and negative plates for the anion of the electrolyte—these attractions being measured by the combining heats of the attracting substances. In this connexion Lodge thus replies to the question, Why is the force of a zinc-iron battery less than that of a zinc-copper or zinc-platinum? :—

"If we picture to ourselves the actual forces in action we shall get a kind of answer indicated to us. In a zinc-iron cell the E.M.F. is due to the zinc pulling at oxygen harder than the iron does; but, since the iron does pull too, with no inconsiderable strength, the balance of force is not so great as if the iron were replaced by copper, which pulls less, or by platinum, which barely pulls at all until it is coated and alloyed with hydrogen. This answer cannot be considered as complete...." ‡ Then follows a discussion of some of the interfering conditions.

We note here that the electromotive force of the cell is decreased by a mere *attraction* of the copper for the anion

* Phil. Mag. [5] xix. p. 208.

† Phil. Mag. [5] xxii. p. 213. Compare also Herroun, Phil. Mag. [5] xxvii. p. 209; and Braun, Czapski, Jahn, and others in recent numbers of Wied. *Ann.*, who refer to points, however, rather beyond the scope of the present paper, which treats mainly a more elementary view of the question.

‡ Phil. Mag. [5] xix. p. 344.

(oxygen) and not by any actual continuous combination of these substances*.

4. The above quotation from Lodge calls to mind a passage in Sprague's 'Electricity,' p. 334, where he speaks of "the struggle between the two metals for the possession of the sulphuric radical."

Sprague evidently pictures the molecules of H_2SO_4 as arranged in polarized molecular chains by the superior attraction of the zinc for the SO_4 radical,

Zinc SO_4H_2 SO_4H_2, &c.

In much the same way Faraday pictured the molecular arrangement "along the axis of power superinduced by the current" in a decomposing electrolyte†. In thinking of the action in the cell I provisionally picture the process in a similar way, and regard the degree or intensity of this molecular polarization as having in some way a relationship to the electromotive force. The transformation of chemical potential energy into current seems always a concomitant of a two-endedness in one of the acting bodies—the electrolyte. There is of course the familiar hypothesis which explains everything, simply by saying that the anion has a negative and the cation a positive charge; but I am inclined to think this says too much, and, to use an expression of Professor G. F. Fitzgerald's, makes "what is known to be complicated appear unreally simple" ‡.

5. On either view, however, any chemical attraction of the negative plate for the cation would increase the electromotive force of the cell. It appears to do so where the negative plate consists of a high oxide like MnO_2 or PbO_2. In what follows an attempt is made to throw some light in the first place on the question—

Under what conditions does a chemical attraction between the negative plate and cation influence the electromotive force of the cell?

6. It follows also from the hypothesis, § 4, that any possible attraction of the positive plate for the cation might also have an effect on the electromotive force; but this point has not, so far as I know, been as yet considered, doubtless because in the

* After this paper had been sent in, Dr. Lodge kindly referred me to memoirs by Bosscha (Pogg. *Ann.* ciii. p. 517) and others, and notably a paper by Sir William Thomson (Math. and Phys. Papers, i. p. 503), from which it would appear that in certain cells the affinity of the negative plate for the anion of the electrolyte is connected with a local conversion of available chemical energy into heat, thus reducing the E.M.F.

This is in agreement with what has been said regarding the dependence of E.M.F. on the relative attractions of the two plates for the anion.

† Exp. Res. i. p. 149, and plate iv. figs. 53, 54.

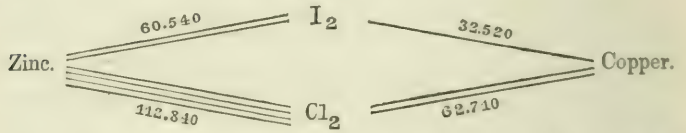
‡ B. A. Report 1890, Discussion on Theory of Solution, p. 19.

cells hitherto examined no such attraction has existed, since the cation was either hydrogen or a metal with no affinity for the positive plate employed. It was therefore proposed in the second place to take up the question—

In what way, if any, does a chemical attraction between the positive plate and the cation influence the electromotive force of the cell?

7. To experiment on these questions it was proposed to replace the hydrogen cation by some substance having an appreciable combining heat with both positive and negative plates. Iodine and bromine in combination with chlorine suggested themselves. The former was first tried, and one form of cell produced would then be represented in the diagram (fig. 1), where the relative attractions between the substances concerned (as measured by their combining heats) are indicated roughly by the number of the lines between each pair. The numerical values of the combining heats (including heat of aqueous solution) are also marked, that for copper and iodine as cuprous iodide, since the cupric salt is unknown in the free state.

Fig. 1.



8. *Iodine monochloride*, ICl, a heavy dark liquid giving off irritating fumes, was obtained from Hopkin and Williams, Hatton Garden, who stated it to be fairly pure. It conducts the current very well, as shown by the following experiment. Two platinum wires were sealed side by side into a tube so that their ends projected from its end at about half a centimetre apart. When connected in circuit with two Fuller cells and a galvanometer they were immersed (with precautions as to cleanliness) alternately in the chloride and in a 10-per-cent. solution of sulphuric acid. The iodine chloride conducted considerably better than the dilute acid.

9. With zinc and platinum plates the chloride acted as an electrolyte, forming a cell with an electromotive force on open circuit of about $1\frac{1}{2}$ Daniell, and giving a current when the circuit was closed. The zinc, however, became coated with a solid black deposit (probably iodine) and a higher electromotive force was given by the chloride in solution.

10. When iodine monochloride is added to water the following reaction takes place*:—

$$20ICl + 5H_2O = I_2O_5 + 10HCl\,ICl + 4I_2.$$

* Schutzenberger, *Comptes Rendus*, lxxxiv. p. 389.

The resulting solution therefore contains iodic acid and the double chloride of hydrogen and iodine, which is stable in water. If, however, the iodine chloride contains in addition to the mono- a higher chloride, and there is sufficient chlorine present to form the double chloride HCl . ICl, no iodine is precipitated and only iodic acid and the double chloride are formed. The first portion of iodine chloride I obtained, and from which the aqueous solutions were made, was probably of this kind. The makers (Irish) stated that it probably contained ICl_3. It was in red-brown crystals, and left only a slight yellowish residue on dissolving in water. Its solution will be referred to for convenience as iodine-chloride solution, see § 15.

11. When electrolysed between platinum poles it deposited iodine at the cathode, sometimes in long filaments, and gas at the anode. When a gradually increasing E.M.F. was applied to the platinum poles, it was found that the ratio of the electrolysing current to the applied E.M.F. began to increase very rapidly at about ·12 D., which corresponds nearly with the ratio of the combining heat I, Cl to the heat equivalent of the Daniell, and indicates the beginning of regular decomposition of that compound. The small current at lower E.M.F.s may readily be connected with the electrolysis of impurities in the solution or the action of dissolved oxygen. The ratio of the current to the applied E.M.F. is considerably greater after ·2 D. till ·25 D., where the experiment ended. The corresponding curve is shown in fig. 3, p. 458.

On testing the secondary E.M.F. of this arrangement, it was found that immediately on removing the applied E.M.F. the electrometer deflexion decreased (rapidly at first) to a point of moderate permanence which varied with the previously applied E.M.F. and current that had passed. It indicated a secondary E.M.F. which (as would be expected from the low combining heat I, Cl) was small and did not in any case exceed ·2 D.

When an intermediate tapping pole was used to test the secondary E.M.F. at the anode and cathode separately, it was found that the principal and more permanent effect was at the anode (from the chlorine probably), whereas that at the cathode was only from ·1 to ·2 of the whole and more evanescent. This might *à priori* be expected, since iodine is not a conductor nor very soluble in the liquid, nor is it likely to alloy with the platinum by occlusion like hydrogen, but simply forms a loose deposit not well adapted to take any further part in electrolytic action.

12. A strip of zinc immersed in the saturated solution was scarcely attacked at first, but merely caused a slight whitish deposit (? iodate of zinc, compare § 25). Afterwards iodine

precipitated on it. Zinc immersed in the dilute solution immediately received a brown deposit of iodine—the zinc no doubt combining with the chlorine. Some gas also, no doubt hydrogen, was evolved at the zinc, especially in a moderately dilute solution, where the action was more rapid. That the zinc in this case should not combine with all the iodine nascent at its surface is remarkable. Does it suggest a polarization of the ICl molecules in which the chlorine end is attracted and the iodine end turned outwards? After a time the iodine deposited in long thin threads. These grew down from the under surface of the zinc with considerable rapidity, giving a curiously animated appearance to the process.

13. The following modification of this experiment is also interesting. When dilute iodine-chloride solution was carefully poured on to strong zinc-chloride solution, there was formed at the dividing line a narrow well-defined brown band which looked like deposited iodine.

I wished to try if the immersion of metallic zinc in the zinc-chloride solution would increase this, and arranged the solutions in the opposite limbs of a V-tube, suspending a piece of sheet zinc in the zinc chloride. The iodine-chloride solution mixed rather quickly with the zinc chloride. In one case, in a flat V-shaped cell, whose limbs were 6 centim. long, I observed that it did so by eddying in long striæ down, round the bend of the tube, and up on the other side. The comparatively rapid motion of these striæ first down and then up through the zinc chloride was very striking. I do not find a ready explanation of it.

In about an hour the zinc-chloride solution had taken a uniform brown tint, and then a black cloud with a curiously sharply defined lower edge formed at the bend of the tube about 2 centim. from the lower end of the zinc. Under the microscope this was seen to consist of minute acicular double-pointed black crystals, probably iodine. It is remarkable that although the zinc in this form of experiment is enveloped by the brown solution, almost none of the iodine crystals are deposited on it as in the case of § 12 ; but in about a week or two there are deposited on the glass, usually at some distance from the zinc, very pretty crystals of iodine.

In one case where a rather dilute iodine-chloride solution had been used, after eight weeks a very fine group of pointed crystals one or two centim. long (a kind of iodine tree) formed in the limb of the tube opposite to that containing the zinc. These formed in a beautiful brown-crimson solution, consisting probably of iodine dissolved in zinc-iodide solution.

In this particular form of experiment the action takes place slowly. The zinc seems to combine chiefly with the chlorine,

A

B.

Fig. 2.—Iodine crystals formed in experiment § 13. From photomicrographs, and magnified about 25 diameters.

but also to some extent with the iodine, the solution of zinc iodide so formed dissolving some reduced iodine to form the brown-crimson solution frequently accompanying the action. It is possible the deposition of the iodine crystals, almost invariably at a distance from the zinc, points to the existence of a polarized molecular chain like that figured by Faraday as connected with electrolytic action and referred to before, § 4.

14. When the zinc was connected to a strip of platinum, also dipping in the iodine-chloride solution, the iodine deposited partly on the platinum and a cell was formed as at 2, Table I.

For obvious reasons this cell differs from those in which hydrogen as cation is evolved in the free state in that it recovers its original electromotive force almost immediately after temporary short-circuiting. Compare § 11.

15. From the observations (§§ 10, 11, 12) and from thermochemical considerations we may, I think, conclude that, of the compounds present in the dilute solution, ICl is the chief, if not the only, one primarily concerned in the electrolysis, and the one on which the character of the cell depends.

16. The electromotive force of cells containing ICl in this solution and otherwise are given in Table I. The forms of cell tested contained one, two, or three electrolytes in series between the positive and negative plates. The affix "Aq" signifies an aqueous solution. This was in all cases saturated, or nearly so, except those in column 4, and also No. 2, Table I. The liquids were contained in a V-tube of the ordinary kind if their respective specific gravities admitted of this arrangement. If not, an inverted V-tube (Λ) was used with an opening at its apex. The metals in wires or strips (not specially pure) were fixed in corks in its ends. The electromotive force was estimated by comparison of the deflexions produced in a Thomson Quadrant Electrometer by the experimental cell and by a standard Daniell (pure copper in saturated copper-sulphate solution and pure zinc in dilute solution of zinc sulphate), which would, according to Dr. C. R. Alder Wright's calculation*, have a force of about 1·13 volt. Where several values for one cell are given, each is the result of a separate and distinct experiment.

17. *Bromine chloride*, BrCl, gives off exceedingly irritating fumes, and is therefore very difficult to work with. Most of the experiments were made with a purchased sample, which was of a reddish-brown colour. As it is rather unstable, in order to check the first results a fresh quantity was subsequently made by passing dried chlorine through bromine

* Phil. Mag. [5] xiii. p. 284.

in a U-tube in ice and brine. After the liquid had increased considerably in volume, and absorption of chlorine appeared to have ceased, a part was transferred to a dried stoppered bottle in ice and brine, and the rest mixed with distilled water to form the saturated solution. The results obtained with this freshly-made chloride were quite similar to those with the purchased substance, except that the latter left an undissolved residue when added to water, apparently bromine.

18. Dry bromine chloride does not conduct the current. This is remarkable, considering its great likeness to the corresponding iodine compound. Two platinum wires sealed in separate glass tubes were connected up in circuit with a very sensitive reflecting-galvanometer, and cells giving an electromotive force of 5 volts. On immersing the projecting ends of the wires in the chloride (either the purchased substance or that freshly prepared and kept in the freezing-mixture) I could not, with certainty, detect the smallest deflexion. If the wires were allowed to touch the glass sides or bottom of the bottle under the liquid, there was a deflexion of several centimetres on the scale. I believe this was probably due to the formation on the glass surface of a conducting film of hydrated chloride from moisture on the glass. The effect was less if the glass vessel had been very carefully dried just before. A solution of bromine chloride in benzol is also nonconducting, and the same effect occurs on touching the glass with the wires.

19. When dry, bromine chloride was arranged as the electrolyte of a voltaic combination with zinc and platinum plates; there is, as would be expected, no current observable, and when these metals were carefully insulated with paraffin and kept from touching the glass under the liquid, there was only a comparatively small and irregular deflexion produced in the electrometer.

20. Bromine chloride, when added to water, forms a hydrated chloride, and when the aqueous solution was electrolysed between platinum poles, gas was given off from both anode and cathode, and the liquid lost its colour. The positive pole tarnished very soon, but neither smell nor colour of free chlorine or bromine was detected. Probably hydrochloric and hydrobromic acids were formed. A positive pole of carbon rod partially disintegrated, and the negative platinum blackened after some time. When a gradually increasing E.M.F. was applied to the platinum poles immersed in the aqueous solution, the ratio of current to applied E.M.F. became sensibly constant at about ·01 D. The heat of combination Br, Cl is ·012 of the heat-equivalent of the action in the Daniell. The curve BrCl

(fig. 3) is from this experiment. The scale is too small to show the part of the curve before decomposition of BrCl may be assumed to begin.

The secondary E.M.F. of this arrangement is, as might be expected, still smaller than that for ICl. In the course of the experiment none was detected with up to as much as ·1 D. applied E.M.F., and the highest secondary E.M.F. observed was under ·05 D. after an applied E.M.F. of $2\frac{1}{2}$ Daniells.

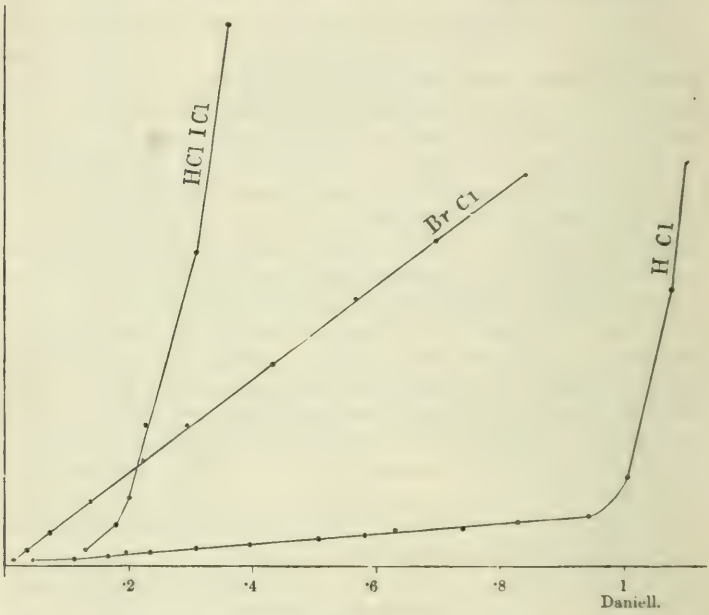


Fig. 3.—Electrolysis of Aqueous Solutions of Hydrogen-Iodine Chloride, Bromine Chloride, and Hydrochloric Acid. Abscissæ correspond to electromotive force in parts of a Daniell; ordinates to current as measured by deflexions of a reflecting-galvanometer (the larger values are about 5 per cent. too large on this instrument).

The hydrochloric-acid curve is for a dilute solution, and is given for comparison with the others. Regular electrolysis begins a little under 1 D. The secondary E.M.F. was, of course, much greater than in the other cases. For BrCl the sensitiveness of the galvanometer was less than for the others, giving a more horizontal line.

21. When a zinc-platinum couple was immersed in the aqueous solution gas was evolved from both metals, and the liquid gradually became colourless without the appearance of any bromine.

In testing the electromotive force of combinations of this electrolyte with various metals &c., the same apparatus and

method were employed as with iodine chloride. The results are given in Table II. The BrCl aqueous solution was saturated and all the others were strong solutions.

22. A number of tentative experiments were made with chlorides of sulphur and phosphorus &c., in attempts to constitute cells in which the chlorine might combine with a positive plate of zinc or other metal, and the sulphur or phosphorus be oxidized by an appropriate oxidizing cathode. The following substances were tried between zinc and platinum plates or zinc and manganese dioxide. They are all, however, almost, if not quite, nonconductors, and it was therefore impracticable to measure definitely their electromotive forces. They appeared to be all considerably under 2 Daniells.

Sulphur chloride, S_2Cl_2.
Same dissolved in carbon bisulphide.
Same after passing dried chlorine into it until it assumed the red-brown colour of SCl_2.
Double chloride of tin and sulphur, $SnCl_4 2SCl_4$.
Phosphorus trichloride, PCl_3.
Same dissolved in benzol.
Same after passing hydrochloric-acid gas through it.
Double chloride of iodine and phosphorus, $PICl_6$, dissolved in phosphorus trichloride, PCl_3.
Phosphorus iodide, PI_2, in carbon bisulphide, CS_2.

23. In Tables I. and II. the values under the head of Theoretical Electromotive Force (except 18 and 20) are obtained by taking the difference of the combining heats, in aqueous solution, of the positive and negative plates with the anion of the electrolyte, chlorine (Cl_2) subtracting twice that of iodine chloride (I, Cl), or bromine chloride (Br, Cl), and dividing by the thermochemical value of the Daniell taken as 50,130.

If P=positive plate, N=negative plate, A=anion, and C=cation, and using the comma-divided symbols as signifying their respective heats of formation, the theoretical electromotive force E_1 will be

$$E_1 = \frac{P, A - A, C - A, N}{50{,}130}.$$

The heats of combination are, with one exception, Thomsen's, taken from the tables in Muir and Wilson's 'Thermal Chemistry.'

24. In comparing the observed and theoretical values, it is to be noted that in the latter no account is taken (except in 18 and 20) of the combining heat of the cation (iodine or bromine) with either positive or negative plate, and the

TABLE I.—Iodine-Chloride Cells.

	Positive Plates (P).	Electrolytes (A and C).			Negative Plate (N).	Value of Electromotive Force in terms of Daniell Cell.	
						Observed.	Theoretical. $\frac{P, A-A, C-A, N}{50{,}130}$
1.	Zinc.	.....	ICl	.....	Platinum.	1·46, 1·4	2·02
2.	,,	.....	ICl Aq	.....	,,	1·7, 1·7	2·02
3.	,,	$ZnCl_2Aq$	,,	.....	,,	1·77, 1·8, 1·9, 1·7, 1·85	2·02
4.	,,	ZnI_2Aq	,,	.....	,,	1·8	2·02
5.	,,	$ZnCl_2Aq$	,,	ZnI_2Aq	Zinc.	0	0
6.	,,	.....	,,	.....	Copper.	·9	·75
7.	,,	$ZnCl_2Aq$	,,	.....	Iron.	·7, ·92	·024
8.	,,	,,	,,	.....	Cadmium.	·35	·098
9.	Magnesium.	$MgCl_2Aq$	,,	.....	Platinum.	2·6, 2·5, 2·5, 2·6	3·5
10.	,,	,,	,,	HClOAq	,,	2·9, 2·9	
11.	Potassium Amalgam.	K_2Cl_2Aq	,,	.....	,,	2·8	2·44 or 3·8
12.	Zinc.	.....	ICl with Benzol	.....	,,	1·5	

TABLE II.—Bromine-Chloride Cells.

	Positive Plate (P.).	Electrolytes (A and C).			Negative Plate (N).	Value of Electromotive Force in terms of Daniell Cell.	
						Observed.	Theoretical. $\frac{P,A-A,C-A,N}{50,130}$.
13.	Zinc.	.....	BrCl	.....	Platinum.	Variable.	
14.	,,	.....	BrClAq	.....	,,	1·9, 1·9	2·23
15.	,,	$ZnCl_2Aq$	,,	.....	,,	1·96, 1·98, 1·94	2·23
16.	,,	,,	,,	.....	Copper.	·75	·98
17.	,,	,,	,,	$CuCl_2Aq$	,,	·83, ·87	·98
18.	,,	,,	,,	$CuBr_2Aq$	,,	13·4, 1·17	1·4
19.	,,	,,	.....	$CuCl_2Aq$	,,	·96	·98
20.	,,	,,	.....	$CuBr_2Aq$	,,	1·14	1·4
21.	,,	,,	BrClAq	.....	Mercury.	·9	1·03
22.	,,	,,	,,	.....	Thallium.	·33, ·43, ·62	·69
23.	,,	,,	,,	.....	Thallium Amalgam.	·6	·69
24.	Thallium.	.....	,,	.....	Platinum.	1·4	1·5
25.	Magnesium.	$MgCl_2Aq$	,,	.....	,,	2·86, 2·7	3·7
26.	,,	,,	,,	.....	Thallium.	1·26	2·1
27.	Potassium Amalgam.	.....	,,	.....	Platinum.	3·0, 2·8	2·6 to 4·01
28.	,,	.....	,,	.....	Silver.	2·0	1·47 to 2·86
29.	,,	.....	,,	K BrAq	,,	1·6	
30.	Zinc.	$ZnCl_2$ Ether.	BrCl Ether.	.....	Platinum.	1·2	

general approximate agreement of the two values points to this as probably the correct method, notably in cases 1, 2, 3, 4, 5, 14, 15, 17, 19, 21, 24, and less distinctly in 6, 11, 16, 27, 28.

In considering the discrepancies between the theoretical and observed values, and the cases where factors besides those mentioned above come in, the following may be noted. The heats of solution of ICl and BrCl are not available. If positive, these would decrease the theoretical values. As the heat of combination for platinum chloride is not available, the theoretical values where platinum forms the negative plate are somewhat too high.

25. The observed forces of those cells with negative plates of iron and cadmium, 7 and 8, are much higher than the theoretical. Both these metals coat themselves at first in the strong solution with a yellowish-white deposit, which may act as a protective layer in the same way as the film of oxide on "passive" iron is believed to do. Professor Letts was kind enough to examine this deposit from the iron, and found it to be iron iodate. Zinc also in very strong iodine-chloride solution deposits a little light-coloured powder, and both iron and zinc are less positive in strong than in moderately dilute solution, the differences in both cases being about ·4 Daniell.

In 10, the heat of oxidation of iodine to HIO_3 probably comes in; but it seems difficult to estimate even approximately the theoretical value for this cell. "Lithanode" (said to be chiefly peroxide of lead) as negative plate instead of platinum also increased the E.M.F. of the ICl cell by ·2 D.; but manganese dioxide rather decreased it, as did also, to a less extent, other oxidizing agents, such as platinum that had been a positive pole in dilute sulphuric acid, and platinum immersed in nitric acid.

In 11, if the heat of amalgamation of potassium $2(K, Hg_{12})$ (Berthelot) be subtracted, 2·44 results, otherwise 3·8. The true value apparently may lie between these. A similar consideration applies to 27 and 28.

In the case of magnesium, 9, 10, 25, 26, the observed values are considerably below the theoretical. Wright and Thompson have observed a similar discrepancy in the case of magnesium immersed in its chloride *.

* Phil. Mag. [5] xix. p. 210. Prof. Herroun suggests (Phil. Mag. [5] xxvii. p. 211) that the metal acts on the water and coats itself with hydrogen.

If instead of the thermochemical value for Mg, Cl we take Mg, O, $H_2O - H_2, O + H_2, Cl_2$, the theoretical E.M.F. is reduced by about 1 Daniell and approaches the observed values. A similar explanation may perhaps apply in the case of potassium, 11, 27, 28, instead of that proposed above.

In 12, heat was evolved on adding iodine chloride to benzol. This, no doubt, reduces the available energy of the electrolyte.

26. Regarding the three-fluid cells in Table II., the solutions noted in the fourth column for 18 and 29 were used with the idea that they might protect the negative plate from contact with the chlorine compound, and substitute a bromine combination; in the latter case, for instance, by dissolving the bromide, which is insoluble in water. Nos. 19 and 20 are for comparison with 17 and 18, when the bromine chloride is omitted.

Some other three-fluid combinations were tried, but the reaction in these cells seems very complicated and needs further investigation. In calculating the theoretical values for 18 and 20, however, the combining heat Cu, Br_2 has been subtracted instead of Cu, Cl_2, which gives a result nearer the observed value.

27. Thallium (22, 23, 26) as a negative plate was chosen as the only metal whose heat of combination with bromine is greater than with chlorine; that is, comparing the heat of the insoluble bromide 82,590 with that of the chloride in aqueous solution 76,960, the object being to form a cell where one metal attracted the anion and the other the cation, and note the effect on the observed force. In this particular case it seemed possible that thallium might by attracting the bromine increase the force of the cell in the same way as the oxygen of hypochlorous acid in 10 may be supposed to do by its combination with the iodine. The assumption that this might occur is doubtless at variance with the theory that metals are "electropositive," and therefore could not combine with the bromine, which has here the *rôle* of an "electropositive" body. Still it was thought worth while to try the experiment, which after all, however, is scarcely decisive, since thallium chloride is not very soluble, and has also a negative heat of solution, and therefore perhaps the heat of the anhydrous chloride should be taken. This being 97,160, is greater than that of the bromide 82,590, and would place thallium in the same category as the other metals.

The forces observed with thallium as negative plate are rather variable, owing probably to the difficulty of cleaning its surface from oxide. Probably the higher values are nearest the truth, in which case 22 and 23 would agree with the hypothesis involved in § 22.

I have to acknowledge my indebtedness to Professor Everett for his kind permission and encouragement to work at the Physical Laboratory, Queen's College, Belfast.

Summary of Principal Conclusions.

In calculating the theoretical electromotive force of voltaic cells from thermochemical data the chemical attraction of a haloid cation for the positive plate (measured by its combining heat with this) does not, so far as these experiments tend to show, enter into the calculation. The cation behaves as if inert, like hydrogen or metals in the commoner forms of cell (§§ 23 to 27).

The attraction of the haloid cation for the negative plate, when the latter is a metal (or so-called electropositive element) does also not enter into the calculation, but its attraction for a so-called electronegative element (*e. g.* oxygen) may in certain conditions influence the result (§§ 23 to 27).

The chlorides of iodine and of bromine in aqueous solutions are decomposed by small electromotive forces, corresponding to their small heats of combination, and the secondary electromotive force in these solutions is of the same order (§§ 11, 12).

The electromotive force of cells with iodine- or bromine-chloride solutions as electrolytes is not decreased after temporary short-circuiting. They do not "polarize" like cells containing hydrogen chloride.

Dry iodine chloride is a good conductor and electrolyte (§§ 8, 9).

Dry bromine chloride, a chemically similar body, does not conduct at all (§§ 18, 19).

The chlorides of phosphorus and sulphur and several of their double salts are not electrolytes (§ 22).

LVIII. *On a Method of Determining the Velocities of Propagation of Disturbances in Elastic Media.* *By* W. T. A. Emtage*.

WHEN a disturbance of any sort is travelling through an elastic medium so that all parts of the medium, after the disturbance has passed them, are left at rest, and in the same relative positions as they had before the disturbance reached them, we may investigate the velocity of propagation of the disturbance in a simple manner as follows.

First, consider the momentum generated in any portion of the medium by the entrance of the disturbance into it. This will be proportional to the velocity of propagation. Next, consider the time integral of the forces producing this momentum; that is, find the mean resulting force acting on the

* Communicated by the Author.

part of the medium considered and the time for which it acts. The force will involve the particular elasticity of the medium concerned in the disturbance; and the time will be inversely proportional to the velocity of propagation.

By equating the momentum generated to the product of the force and the time for which it acts, we get an equation by which to find the velocity of propagation.

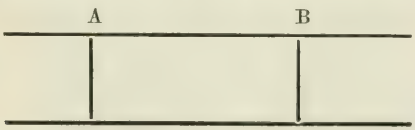
In the case of the propagation of a series of waves, they may be considered as a succession of single disturbances, and the velocity of propagation will be the same as for a single disturbance.

Longitudinal Disturbance.

Suppose a long cylindrical uniform bar of cross section S. Let a compression be created in this bar at one end, and propagated along it from left to right. We may imagine the passage of the compression to take place by supposing each portion of the bar, as soon as the compression reaches it, to press forward on the next adjoining portion and compress it, returning itself to its natural condition, the whole of the bar to the left of the compression being left in its natural condition.

Let E be the Young's modulus of the bar, d its density. Suppose a length x to be involved at each instant in the compression, and let l be the amount of the compression, so that each point of the bar travels forward by a distance l as the compression passes through it. Let V be the velocity with which the compression travels.

Consider two planes A and B drawn at right angles to the bar and fixed in space. Then while the compression is passing across A, the mean pressure at A in excess of that at B is



$\mathrm{E}\frac{l}{x}$. And the time taken for the compression to pass A is $\frac{x}{\mathrm{V}}$.

Thus the momentum generated in the space between A and B is

$$\mathrm{ES}.\frac{l}{x}\cdot\frac{x}{\mathrm{V}}.$$

But in each second a length V of the bar is displaced forward by a distance l. Thus we have for the momentum

generated between A and B, while the compression is travelling between A and B, the expression

$$\mathrm{V}\,l\,\mathrm{S}\,d.$$

Equating these expressions, we get

$$\mathrm{V}^2=\frac{\mathrm{E}}{d}.$$

The same amount of momentum is generated between A and B by the passage of the compression across B, thus leaving the portion A B at rest.

In the same way a rarefaction may be propagated by the successive portions of the bar moving to the left by a distance l. The momentum generated in A B by the passage of the rarefaction across A, and destroyed by its passage across B, is in this case from right to left.

It has been shown, so far, that the disturbance is propagated with a *mean* velocity $\sqrt{\frac{\mathrm{E}}{d}}$. But we may show that each portion of it is propagated with the same velocity, or that it travels unchanged in form, by applying the same considerations to any portion of the disturbance instead of to the whole of it.

Consider a portion of the disturbance of length x to be crossing the plane A with velocity V. Let l be the amount of compression in this portion. l is positive or negative according as the length x is compressed or extended. The passage of this portion across A generates momentum in A B, from left to right, equal to $\mathrm{ES}\cdot\frac{l}{x}\cdot\frac{x}{\mathrm{V}}$. Also the quantity of momentum generated in A B by this passage, supposing the part of the disturbance in front of x to travel unchanged in velocity and form, is $\mathrm{V}\,l\,\mathrm{S}\,d$.

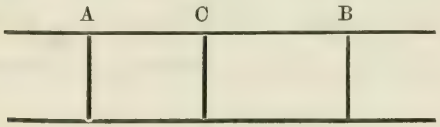
Thus, if we suppose the entire disturbance, of any form, to be moving with uniform velocity $\sqrt{\frac{\mathrm{E}}{d}}$, the forces brought into play at each point are just the necessary forces to keep up the propagation unchanged. With any other velocity of the disturbance, or of any part of it, this would not be the case. This is therefore the velocity of the disturbance, and it travels unchanged in form.

Reflexion of Disturbances.—When a compression, moving from left to right, reaches the free end of a bar, the bar possesses momentum from left to right which is not destroyed.

Thus the successive layers still move towards the right, now starting from the free end. Thus the compression is reflected as a rarefaction. In the same way a rarefaction is reflected as a compression. This is the case of reflexion without change of sign.

When a compression reaches a fixed end, the momentum of the bar, from left to right, is more than destroyed at the end, and a compression is reflected. In the same way a rarefaction is reflected as a rarefaction. This is the case of reflexion with change of sign.

Case of Two Media.—Suppose we have two bars of cross-section S joined end to end, C being the common surface.



Let E_1, d_1, V_1 ; E_2, d_2, V_2 denote the Young's modulus, density, and velocity of wave propagation in the two media. Suppose a compression producing a displacement l to the right to be propagated from left to right in A C. Let this produce a reflected disturbance of A C, causing displacement l' to the right. Then, since the bars on both sides of C return to their natural conditions after the passage of the disturbance, the disturbance transmitted to C B causes displacement $l+l'$ to the right. Now the momentum in the space A B is the same just before and just after the disturbance in A C reaches C. Thus we have

$$Sld_1V_1 = Sl'd_1V_1 + S(l+l')d_2V_2 ;$$

$$\therefore \quad (l-l')d_1V_1 = (l+l')d_2V_2.$$

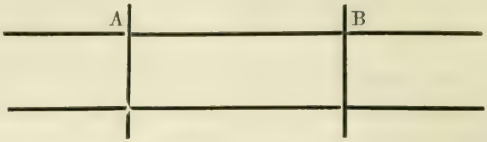
Thus l' will have the same sign as l, or there will be reflexion without change of sign, if d_1V_1 is $> d_2V_2$, or d_1E_1 is $> d_2E_2$.

l' will have the opposite sign to l, or there will be reflexion with change of sign, if d_1V_1 is $< d_2V_2$, or d_1E_1 is $< d_2E_2$.

Transverse Disturbance.

Suppose a uniform bar of cross-section S ; and let M be its rigidity, and d its density. Let a transverse disturbance be sent along it from left to right. Let the disturbance be such that each point of the bar is displaced upwards by a distance l as the disturbance passes it. Let x be the length involved

at any instance in the disturbance. Let V be the velocity of propagation of the disturbance.



Take two planes A and B drawn across the bar.

Consider the momentum generated inside the space A B by the passage of the disturbance into A B.

In the passage of the disturbance across A the mean force acting on A B is $\mathrm{SM}\frac{l}{x}$, and is upwards. And the time for which it acts is $\frac{x}{\mathrm{V}}$. Thus the momentum generated is

$$\mathrm{SM}\frac{l}{x}\cdot\frac{x}{\mathrm{V}}.$$

Also, since a portion of length V is displaced upwards by a distance l in one second, the momentum is

$$\mathrm{SV}ld.$$

Thus we get

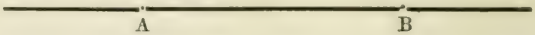
$$\mathrm{V}^2=\frac{\mathrm{M}}{d}.$$

That the disturbance travels unchanged in form may be proved as in the case of a longitudinal disturbance, by showing that when the velocity of each part is $\sqrt{\frac{\mathrm{M}}{d}}$, then the forces called into play at each point are just the necessary forces to maintain the disturbance unchanged.

The case of two media may be investigated as before.

Transverse Disturbance in Stretched String.

Suppose we have a string of which m is the mass per unit length, stretched with a tension T. Let a transverse disturbance be sent along it from left to right. Let the disturbance be such that each point of the string is displaced upwards by a distance l. Let x be the length of the string involved at any instant in the disturbance. Let V be the velocity of propagation of the disturbance.



Take two points A and B on the string.

Consider the momentum generated between A and B by

the passage of the disturbance into A B, which momentum is in the direction of l.

In the passage of the disturbance across A the mean force acting upwards is $\mathrm{T}.\frac{l}{x}$. And the time for which it acts is $\frac{x}{\mathrm{V}}$. Thus the momentum generated is

$$\mathrm{T}\frac{l}{x}\cdot\frac{x}{\mathrm{V}}.$$

Again, we have for the momentum generated the expression

$$m.\mathrm{V}\,l.$$

Thus we get

$$\mathrm{V}^2=\frac{\mathrm{T}}{m}.$$

LIX. *On Manganese Tetrachloride.*

By H. M. Vernon, *Scholar of Merton College, Oxford**.

WHEN manganese dioxide is treated with hydrochloric acid it dissolves with formation of a dark-brown coloured liquid. This liquid evolves chlorine slowly at ordinary temperatures, and at higher temperatures evolution takes place much more rapidly, the solution soon becoming colourless and containing only manganous chloride and hydrochloric acid. Forchammer showed, in 1821, that when this brown liquid is diluted with a large quantity of water, the solution remains clear for a few seconds and then becomes turbid, a mixture of oxides of manganese being precipitated. He also showed that a similar precipitation of oxides takes place when solutions of manganese sesquioxide and manganoso-manganic oxide, Mn_3O_4, in hydrochloric acid, were diluted with water. He did not, however, attempt to arrive at the constitution of the higher chloride of manganese which he supposed to exist in these dark-brown solutions.

W. W. Fisher (Chem. Soc. Journ. 1878, p. 409) endeavoured to show that the dark-brown liquid contains manganese tetrachloride. He did this by delivering from a burette known volumes of the liquid (1) into a solution of potassium iodide, (2) into a large volume of water or, preferably, dilute potassium-acetate solution. If the action of hydrochloric acid upon manganese dioxide is considered to be represented by the equation

$$MnO_2+4HCl = MnCl_4+2H_2O,$$

* Communicated by the Author.

then it is probable that the reverse action of water upon manganese tetrachloride is represented by the equation

$$MnCl_4 + 2H_2O = MnO_2 + 4HCl,$$

while the action of potassium iodide upon manganese tetrachloride will be represented by the equation

$$MnCl_4 + 2KI = MnCl_2 + I_2 + 2KCl;$$

so, from the amount of iodine liberated from the potassium iodide, and the amount of manganese dioxide precipitated, the ratio in which the manganese and available chlorine exist in the brown solution is obtained. This ratio, which from the above equations is required to be 1 : 2, was found experimentally to be almost exactly 1 : 2. Fisher showed that the same ratio of manganese to available chlorine likewise held good for the solution of manganoso-manganic oxide in hydrochloric acid, the reaction taking place on the solution of this oxide in HCl being presumably

$$Mn_3O_4 + 8HCl = 2MnCl_2 + MnCl_4 + 4H_2O;$$

and, arguing from analogy, the action of hydrochloric acid upon manganese sesquioxide would be

$$Mn_2O_3 + 6HCl = MnCl_2 + MnCl_4 + 3H_2O.$$

S. U. Pickering (Chem. Soc. Journ. 1879, p. 654) repeated Fisher's experiments, and in addition made a number of experiments of his own upon the subject. He pointed out that Fisher's experiments only showed that the solution contained a higher chloride of the form Mn_nCl_{2n+2}, and did not prove that this chloride was the tetrachloride. He also showed that it cannot be argued that the chloride Mn_2Cl_6 is not formed on solution of the corresponding oxide in hydrochloric acid, because the oxide precipitated from the solution by water is MnO_2 and not Mn_2O_3; for if it is possible to obtain from the sesquioxide a chloride corresponding to the dioxide, so it is just as possible that the dioxide should be obtained from a chloride corresponding to the sesquioxide, thus—

$$Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.$$

Pickering then endeavours to show that the higher chloride formed by the reaction of manganese dioxide and hydrochloric acid is manganese sesquichloride, and that therefore manganese tetrachloride has no existence. His two arguments for the existence of manganese sesquichloride will be discussed further on.

It appeared to me that, although Pickering in his paper

seemed to demonstrate the existence of Mn_2Cl_6, yet he did not clearly show that the tetrachloride had no existence. Experiments were therefore made with a view to elucidating this question.

If, as Pickering concludes, the action of hydrochloric acid upon manganese dioxide is expressed by the equation

$$2MnO_2 + 8HCl = Mn_2Cl_6 + Cl_2 + 4H_2O,$$

then it is evident that, if such really be the case, when the dioxide is dissolved in hydrochloric acid, half of the total available or loosely combined chlorine present ought to be evolved very quickly, while the other half ought to come off very much more slowly, as manganese sesquichloride only decomposes moderately slowly at ordinary temperatures. Also it would follow that the rate of evolution of the first half of available chlorine should be almost unaffected by the temperature at which the solution takes place; whilst, as Pickering has clearly shown by his experiments, the rate of decomposition of the higher chloride of manganese, whatever it may be, is very much diminished by lowering the temperature, and is correspondingly increased by raising the temperature of solution. In fact, the only ways in which temperature would affect the rate of evolution of the first half of the available chlorine would be that (1) the dioxide would dissolve more slowly at lower than at higher temperatures, and (2) chlorine is more soluble in hydrochloric acid at lower temperatures, and hence less of it would be evolved from the solution even if it might exist in it in the free state.

The Amount of Decomposition taking place in the Dioxide Solution.

Experiments were therefore made to ascertain:—

(1) Whether, on solution of the dioxide in hydrochloric acid, a considerable quantity of chlorine is immediately evolved; and whether, after half the available chlorine has been evolved, the rate of evolution becomes much slower.

(2) To what extent the rate of evolution of the chlorine is affected by lowering the temperature.

The method adopted consisted in drawing a slow current of air through a known quantity of the dioxide dissolved in a measured volume of concentrated hydrochloric acid, which was kept at a constant temperature. The air then passed through potassium-iodide solution. The iodine thus liberated by the chlorine was estimated by titration with standard

sodium-thiosulphate solution. It was accordingly first necessary to see how far the passage of a current of air was capable of removing chlorine dissolved in strong hydrochloric acid. In the table below will be found a series of determinations of the percentage of chlorine removed on that present in the solution, under varying conditions as to temperature, degree of saturation of the hydrochloric acid, volume of air drawn through the solution, and time during which the passage of the air lasted. The air was caused to take up the same temperature as the hydrochloric acid through which it was drawn, by allowing it to first pass through a worm-tube surrounding the flask containing the hydrochloric acid, the whole apparatus being immersed in water or a freezing-mixture, as the case might be.

No. of Exp.	Time of passage of Air.	Volume, in litres, of Air drawn through.	Temperature.	Amount of Chlorine present on the saturating quantity.	Percentage of Chlorine removed.
1.	10 min.	·7	21°	100	87·8
2.	10 „	·7	21	47	77·5
3.	10 „	·7	21	23·1	73·8
4.	10 „	·3	21	72·8	80·0
5.	10 „	·2	−14	100	56·8
6.	15 „	·3	−14	2·4	48·3
7.	50 „	1·0	7	22·1	99·7

It will be seen that in a very short time the greater part of the chlorine is removed from the solution by the passage of the current of air, whether it be moderately fast or slow. In the last experiment, where the current was continued for a longer time, the hydrochloric acid was found to contain only the merest trace of chlorine. As in the experiments to be described below, the current of air was usually continued for two hours or more, it may be concluded that the amount of chlorine removed from the solution of manganese dioxide in hydrochloric acid gives a very good estimate of the amount of chlorine actually set free.

Both anhydrous and hydrated manganese dioxide were used in these experiments. The anhydrous variety was prepared by igniting pure manganese nitrate, washing, and drying at 100° C. It was found to contain almost the theoretical quantity of manganese dioxide (99·2 per cent.). The hydrated variety was prepared by dissolving commercial dioxide in hydrochloric acid, and precipitating by pouring the

solution into water. The precipitate was collected, washed, and dried for sixteen hours at 75° C. Its composition was as follows :—

MnO_2	=	90·77 per cent.
MnO	=	4·21 „
H_2O	=	4·80 „
		99·78

This and other specimens of dioxide were analysed by heating a weighed quantity to redness for about thirty minutes and reweighing on cooling. The amount of available oxygen existing in the oxide, which consists chiefly of Mn_3O_4, is then estimated in the usual way by heating with hydrochloric acid and estimating the chlorine evolved. Separate values of the total manganese and of the water present are thus arrived at. The available oxygen in the dioxide is determined separately.

I. To a weighed quantity (·3069 grm.) of hydrated MnO_2 in a small flask were added 10 cub. centim. of concentrated hydrochloric acid. The flask was immersed in water at 18° C. In fifteen minutes, when ·4 litre of air had been drawn through, 14·2 per cent. of the available chlorine was removed. In forty-five minutes longer 31·7 per cent. more chlorine was removed ; or, in the first hour 45·9 per cent. had been removed. In this time 1·5 litre of air had been drawn through the solution. In the next hour 14·1 per cent. more chlorine was removed, and in the next two hours 10·5 per cent. more. We thus see that, while half the available chlorine had not been removed even after an hour, yet that the amount removed is much greater in the first hour than in the second, and this is greater than in the next two hours. The reason of this will be made evident further on. It should be noticed that, while the amount of chlorine removed is much smaller in the second hour than in the first, yet that in the next two hours it is smaller in about the same proportion; while if Mn_2Cl_6 and no $MnCl_4$ were formed in the solution, we should expect the last half of the chlorine to come off at a more even rate than it does here. Also the first half of the chlorine cannot be said to have been evolved very quickly, as it took over an hour to be removed from the solution.

II. To a weighed quantity (·2819 grm.) of hydrated dioxide in a small flask, surrounded by a freezing-mixture of ice and salt, were added 10 cub. centim. of hydrochloric acid which had previously been cooled to the temperature of the freezing-mixture, viz. −14° C. The air, before bubbling through the liquid, was drawn through a worm-tube immersed in the

same freezing-mixture as the flask. It was found that, after the passage of the current of air had been continued for two hours, 19·1 per cent. of the available chlorine had been removed. In another experiment, at −6°, it was found that 33·8 per cent. was removed in two hours. The manganese dioxide did not appear to be nearly so readily soluble in hydrochloric acid at these low temperatures as it is at ordinary temperatures; for it was found that some of it remained undissolved even at the end of the two hours. It was therefore necessary to ascertain how much of the dioxide had actually passed into solution, as the undissolved dioxide would not enter into the reaction at all. In these experiments at low temperatures, therefore, after the passage of the current of air had been stopped, the liquid in the flask was poured on to a small filter, the filtrate passing into potassium-iodide solution, while the undissolved dioxide remained behind. As the filtering only took a few seconds, only a very small quantity of chlorine would escape from the solution and so not be accounted for.

III. The amount of chlorine removed from a solution of dioxide in hydrochloric acid at −26° C. was then determined. The flask and worm-tube used in the previous experiments were surrounded by a freezing-mixture of crystallized calcium chloride and pounded ice. The vessel containing this being well covered up, the liquid was kept at a uniform temperature throughout the experiment. It was found that in two hours only 1·8 per cent. of the available chlorine had been removed. During this time about 2 litres of air were drawn through the solution. In the former experiments about 2·7 litres of air were drawn through during the two hours.

Another experiment, at −19° C., showed that 12·2 per cent. of chlorine was removed in two hours.

It thus appears that the stability of the dioxide solution is very greatly increased as the temperature is lowered, and so we might expect that at a still lower temperature it would not undergo any decomposition whatever. It would not be possible to try the action of hydrochloric acid on the dioxide at a much lower temperature than −26°, as hydrochloric acid solidifies at −29°, though when it contains chlorine or manganese dioxide in solution it does not solidify till below this temperature.

It might be thought possible that the reason why no chlorine is evolved from the solution is not that it is not actually set free by the reaction of the dioxide and hydrochloric acid, but that it forms a solid hydrate with some of the aqueous hydrochloric acid, and so is not removed from the solution by the passage of the air. That this was not the case

was proved by passing chlorine into hydrochloric acid at $-20°$ for some time, no chlorine hydrate being formed. Indeed, it was found that the addition of even a small quantity of hydrochloric acid to water containing chlorine-hydrate crystals almost immediately destroyed them. Thus chlorine was passed into 10 cub. centim. of water at 2°, chlorine hydrate being very soon formed; when, however, ·5 cub. centim. of hydrochloric acid was added to the water, the hydrate rapidly disappeared. Again, when a solution containing water and HCl in the proportion 6 : 1 was saturated with chlorine at $-9°$, the hydrate was formed; this quickly disappeared when one part more of HCl was added. Lastly, it was found that, when a mixture of water and hydrochloric acid in equal proportions was saturated with chlorine at $-19°$, no hydrate whatever was formed.

It is therefore conclusively shown that when manganese dioxide dissolves in hydrochloric acid, manganese tetrachloride and no free chlorine are originally formed, and that the lower the temperature the more stable does this tetrachloride solution become.

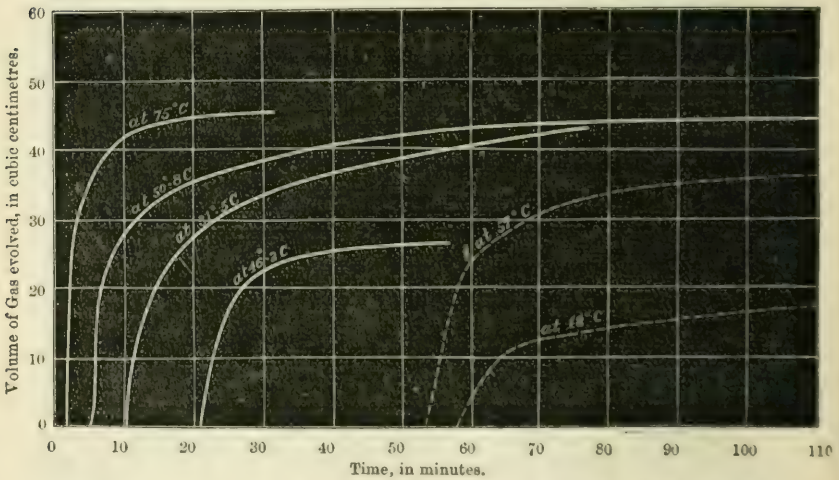
The Rate of Evolution of Chlorine from the Solution.

It is now necessary to ascertain whether, on decomposition of the tetrachloride solution, the sesquichloride or any other intermediate chloride is formed.

If an intermediate chloride, as Mn_2Cl_6, is formed on the decomposition of the tetrachloride, we may reasonably expect that this chloride should be more stable than the tetrachloride. Consequently when a solution containing originally only tetrachloride decomposes, we should expect the first half of the chlorine to come off considerably faster than the last half. At ordinary temperatures the decomposition of the solution is so slow that it would take a day or two before the greater part of the chlorine would be evolved. The variations in the temperature of the atmosphere, and also the impossibility of taking a continuous series of readings of the volume of gas evolved during this time, would render it impossible to arrive at a satisfactory conclusion as to the rate of decomposition of the solution. If, however, the temperature of the solution be raised to above 30°, the rate of evolution becomes much more rapid, and the greater part of the chlorine is evolved in a few hours.

Small weighed quantities (about ·2 grm.) of the dioxide, in both its anhydrous and hydrated forms, were placed in the bulb of a V. Meyer's vapour-density apparatus. This was surrounded by an outer tube of water, which was in turn surrounded by

a large vessel of water kept at a constant temperature throughout the experiment. On the dioxide was poured a volume of concentrated hydrochloric acid, varying from 5 to 10 cub. centim. in different experiments. The temperature of the bath was varied in different experiments from 31°·5 to 75°. Above this temperature the rate of evolution becomes so rapid that it is impossible to measure the volume of gas evolved accurately. The air evolved was collected over water. The volume of the apparatus was very much larger than that of the chlorine evolved; and it was found experimentally that scarcely a trace of chlorine reached the collecting-tube even after several hours. Observations were made at intervals of a quarter or half a minute, or at greater intervals when at the close of an experiment the evolution became much slower. The results obtained are represented diagrammatically in the illustration. Here the ordinates represent the volume of gas evolved in cub. centim., and the abscissæ represent the time in minutes. The first curve represents the rate of evolution at 75° C. It will be seen that the gas is evolved very rapidly, more than half of it coming off in the first minute, while all of it appeared to have come off in half an hour.



The second curve gives the rate of evolution at 50°·8. Here the gas is not evolved so rapidly; even after two hours the evolution did not appear to have quite stopped. The next curve gives the rate of evolution at 31°·5. For this curve each division of the paper represents forty minutes instead of ten minutes. It will be noticed how very much more slowly the gas is coming off here than it did before. Thus it had

not quite stopped even after nearly five hours. The first two of these three curves show that the gas is evolved quite regularly till the last few cub. centim., when the rate of evolution becomes much slower. The reason of this is evidently, that at the points where the forms of the curves change, the greater part of the tetrachloride present has been decomposed into manganous chloride and chlorine, and that most of the gas which is evolved after this is evolved from the hydrochloric acid in which it is mechanically dissolved. Chlorine was found to have about the same degree of solubility in hydrochloric acid as in water; at 50°, therefore, it dissolves ·9 vol. and at 75° ·2 vol. of chlorine. At the commencement of the evolution of this "residual" chlorine the acid will be considerably supersaturated with it, but the greater part present will be expelled from the solution in the course of an hour or two. We may therefore expect the volume of "residual" gas to bear some proportion to the temperature as well as to the volume of hydrochloric acid employed. In the experiments of the first two curves, representing the evolution at 75° and 50°·8, 5 cub. centim. of hydrochloric acid were used. We see, however, that the volume of residual gas is much greater at the lower temperature than at the higher, it being about 10 cub. centim. in one case and only 4 cub. centim. in the other. In the curve representing the evolution at 31°·5, 8 cub. centim. of hydrochloric acid were used. Here the rate of decomposition of the tetrachloride is so slow that it is not possible, from the form of the curve, to tell where the greater part of it has undergone decomposition and where residual gas begins to be evolved. They evidently overlap each other, so as to form one regular curve. Though the form of this curve is regular, it nevertheless shows that the rate of decomposition of the tetrachloride solution is much slower at the end than at the beginning of the experiment, after allowing of course for the amount of tetrachloride actually existing in the solution. The reason of this will be made evident further on. It will be noticed how much more slowly the chlorine comes off from the solution when it is left alone than when a current of air is drawn through it, as in the previous experiments, allowance being made for the difference of temperature. Thus at 18° it was found that in four hours 70·5 per cent. of the chlorine was removed by a current of air from the dioxide solution, whilst here only about 85 per cent. of chlorine was evolved from the solution in four hours at 31°·5. The reason of this is partly that a certain amount of the chlorine remains dissolved in the solution without being evolved, but it is also probable that the passage of the current

of air has a certain amount of decomposing effect on the solution.

Other determinations of the rate of evolution of chlorine were made at temperatures between the extremes given above, namely, at 32°, 43°, 48°·2, 57°, 59°, and 63°. The curves were in all cases quite regular, until the last few cub. centim. of gas were being evolved, when their form changed suddenly in the same way as those given above. It was accordingly not thought necessary to represent them here. In the experiment at 59°, when only 3 cub. centim. instead of 5 cub. centim. of hydrochloric acid were used, only about 3·5 cub. centim. of residual gas were evolved.

It is thus evident that when the tetrachloride solution undergoes decomposition, no intermediate chloride as Mn_2Cl_6 is formed, but it decomposes regularly into $MnCl_2$ and Cl_2. If it were possible that the sesquichloride were formed at one temperature, and that it happened to be just as unstable as the tetrachloride at this particular temperature, yet it is scarcely possible that through a range of temperature of more than forty degrees, the tetrachloride should always decompose with formation of an intermediate chloride which possessed just the same degree of stability as itself.

The fourth curve in the figure represents the rate of evolution of chlorine from a specimen of manganese oxide containing 45·33 per cent. MnO_2 and 10·9 per cent. water. It therefore consists chiefly of Mn_2O_3. It will be seen that the curve representing the rate of evolution of gas is regular, and similar to the former curves. If, now, it be supposed for the time being that the sesquioxide on dissolving in hydrochloric acid forms the sesquichloride, it would follow from the fact of this curve being regular that no chloride as Mn_3Cl_8, intermediate between Mn_2Cl_6 and $MnCl_2$, is formed in its decomposition.

The two dotted-line curves represent the rate of evolution of chlorine from a solution of manganoso-manganic oxide, Mn_3O_4, in hydrochloric acid. This Mn_3O_4 was prepared by heating some of the precipitated dioxide in the blowpipe flame for a considerable time. The form of these curves is similar to that of the others, only that more residual chlorine is evolved. This is due to the fact that more hydrochloric acid was added; for nearly three parts of this oxide have to be dissolved to give the same volume of chlorine as one part of the dioxide. Thus in the curve at 57°, where 8 cub. centim. of hydrochloric acid were used, there are about 9 cub. centim. of residual gas, while in the curve at 48°, with 7 cub. centim. of hydrochloric acid, there are also about 9 cub. centim., or nearly half of the total volume of gas evolved. It is thus con-

clusively proved that the change in the form of the curves is due to the evolution of this residual gas, and not to the decomposition of a more stable higher chloride of manganese.

These results, therefore, show that when any of the oxides of manganese, MnO_2, Mn_2O_3, and Mn_3O_4, dissolve in hydrochloric acid, the only higher chloride produced is manganese tetrachloride. The equations for the solution of manganese sesquioxide and manganoso-manganic oxide in hydrochloric acid must therefore be :—

$$Mn_2O_3 + 6HCl = MnCl_4 + MnCl_2 + 3H_2O.$$
$$Mn_3O_4 + 8HCl = MnCl_4 + 2MnCl_2 + 4H_2O.$$

Discussion of the Results obtained by Pickering.

It is now necessary to see if it is possible to reconcile these results with those obtained by Pickering.

The first of his two arguments for the existence of manganese sesquichloride and the non-existence of the tetrachloride, is, that if the chloride formed by the solution of the dioxide in hydrochloric acid is $MnCl_4$, then it can make no difference to the amount of this chloride obtained whether the solution be performed in pure hydrochloric acid, or in acid containing a quantity of manganous chloride ; whereas, if the chloride be Mn_2Cl_6, then by performing the solution of the dioxide in the presence of a sufficient quantity of manganous chloride we might succeed in converting the whole of the oxide, together with some of the dichloride added, into the higher chloride ; so that on decomposing it with water, we should get as much dioxide precipitated as was dissolved, thus :—

$$MnO_2 + 4HCl + MnCl_2 = Mn_2Cl_6 + 2H_2O,$$
$$Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.$$

Otherwise, if no dichloride were added to the acid, we should not be able to obtain in the precipitate more than half of the dioxide dissolved, thus :—

$$2MnO_2 + 8HCl = Mn_2Cl_6 + 4H_2O + Cl_2,$$
$$Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.$$

Accordingly, Pickering made a series of experiments in which given weights of the dioxide were dissolved in hydrochloric acid in the presence of varied proportions of manganese dichloride, and the solutions thus formed precipitated with water, and the dioxide in the precipitate estimated. He found that when no manganese chloride was added, 45 per

cent. of the original MnO_2 was recovered. When one molecule of $MnCl_2$ was added, 80 per cent. of MnO_2 was recovered; and with six molecules of $MnCl_2$, 95·5 per cent. was recovered. When the results of ten determinations with proportions of manganese chloride varying between these limits were represented diagrammatically, it was found that up to the addition of one molecule of $MnCl_2$ the curve representing the amount of MnO_2 recovered was a straight line ; after this point the form of the curve changed suddenly, the ratio of MnO_2 recovered to molecules of $MnCl_2$ added being considerably less than before. Pickering considers this to conclusively show that the tetrachloride has no existence, and also that the higher chloride formed is Mn_2Cl_6.

On examination it will be found that this argument neither proves the non-existence of the tetrachloride nor the existence of the sesquichloride. Thus, it can be shown mathematically that supposing $MnCl_2$ and the solution of the dioxide in hydrochloric acid react as Pickering supposes, the form of the curve up to the addition of one molecule of $MnCl_2$ will not be a straight line, but will be to a certain extent curved. Also, he says that the form of the curve changes suddenly after one molecule of $MnCl_2$ has been added. He forgets, however, that there is not one molecule of $MnCl_2$ present, but 1·132 molecule, for the specimen of dioxide used he showed to contain 85·15 per cent. MnO_2 and 9·36 per cent. MnO : this MnO, on addition of hydrochloric acid, would of course form $MnCl_2$, and this was not taken account of when the rest of the $MnCl_2$ was added. He found that the addition of one molecule of $MnCl_2$ raised the amount of MnO_2 recovered from 45 per cent. to 80 per cent.; the addition of ·132 molecule would accordingly raise it 4·62 per cent. He found the form of the curve to change, therefore, after a point where 80 per cent. of the dioxide was recovered, while according to his argument it should have been after 75·36 per cent. was recovered. Also he would only have recovered 40·36 per cent. of the original MnO_2, if pure dioxide had been used. These discrepancies may be due to the conditions of solution and precipitation of the dioxide not being kept quite the same for different experiments. It would seem, therefore, that all that this curve can with certainty be taken to show is, that the amount of MnO_2 recovered is increased by the addition of $MnCl_2$ to the solution, the amount of this increase being in proportion less and less with each addition of $MnCl_2$. This does not, however, show that when the dioxide dissolves in hydrochloric acid, the sesquichloride and free chlorine are formed ; it only shows that manganese tetrachloride is more stable in the presence of

manganous chloride, just as, in an analogous case, Wurtz showed that phosphorus pentachloride dissociated to a very much slighter extent when volatilized in vapour of phosphorus trichloride than when volatilized alone. In the case of the solution of manganese dioxide in hydrochloric acid, we have unstable molecules of the tetrachloride continually dissociating into manganous chloride and two atoms of chlorine, and the molecules of manganous chloride thus formed continually, but to a smaller extent, uniting with the atoms of chlorine present, to form the tetrachloride again. If, therefore, a large excess of $MnCl_2$ is present, it is obvious that much less of the chlorine formed by the decomposition of the tetrachloride will escape recomposition with $MnCl_2$ molecules, and so less chlorine will be evolved from the solution. Also it is evident that the addition of the first molecule of $MnCl_2$ will cause a greater increase in the amount recovered than the addition of the second and other molecules, but at the same time a curve expressing the amount recovered for each addition of $MnCl_2$ would not change its form suddenly after the addition of the first molecule.

We thus arrive at an explanation as to why the amount of chlorine removed from a solution of the dioxide in hydrochloric acid was considerably greater in the first hour than in the second, and this was greater than in the next two hours. It is because that, as the original $MnCl_4$ begins to be decomposed, a corresponding quantity of $MnCl_2$ is formed. Therefore, the more $MnCl_4$ decomposed, the more $MnCl_2$ is formed, and so the more stable becomes the remnant of $MnCl_4$ still left undecomposed. The same explanation also applies to the curve for the rate of evolution of chlorine from the dioxide solution at 31°·5.

It might be concluded that if the dioxide be allowed to dissolve in hydrochloric acid saturated with chlorine, less decomposition would, for a similar reason, take place, and therefore more dioxide would be recovered. In practice, it was found that the amount of MnO_2 recovered was raised scarcely at all by this means. This is probably due to the fact that $MnCl_2$ is unable to recombine with molecules of chlorine to form the tetrachloride, but only with nascent chlorine set free by other decompositions of $MnCl_4$ molecules.

It was found experimentally that hydrochloric acid containing $MnCl_2$ in solution did not dissolve any more chlorine even at $-32°$ than hydrochloric acid alone, and also the solution was not darkened in colour. No higher chloride could therefore have been formed. It is scarcely possible to try the action of nascent chlorine upon manganous chloride

except in the tetrachloride solution; but as the nearest approach to this, the action of chlorine gas upon it when mixed with cobalt sesquichloride in a hydrochloric acid solution, was tried, and also the action of lead tetrachloride in the acid solution. No darkening in the colour of the solution took place, however.

Pickering's second argument for the existence of manganese sesquichloride is as follows :—"Seeing that a rise in temperature materially decreases the stability of the higher chloride, whilst a reduction of temperature increases its stability, then, by performing the solution of the dioxide at a sufficiently low temperature, there could be no reason why all of it should not be converted into the higher chloride, if this higher chloride is $MnCl_4$, and should be subsequently precipitated entirely as dioxide. If, however, the higher chloride formed were Mn_2Cl_6, it would only be possible to obtain 50 per cent. of the dioxide used." A series of experiments was therefore made, similar in every respect, except that the temperature of solution of the dioxide was varied. It was found that when the solution was performed at 10°, 45·5 per cent. of the MnO_2 was recovered. This amount was only increased to 47 per cent. when performed at −20°. Above 10° the percentage recovered began to decrease more rapidly, till at 61° only 9 per cent. was recovered. That is to say, if pure dioxide had been used, only at the most 42·36 per cent. instead of 45·5 per cent. of the original dioxide used would have been recovered.

Experiments were therefore made to see if it were not possible to recover more than this percentage when pure dioxide was used, or a correspondingly larger percentage when dioxide containing some MnO was used. In these experiments a weighed quantity of the dioxide was shaken about with a measured volume of concentrated hydrochloric acid in a flask surrounded by a vessel of water to keep the temperature constant. Five minutes was generally allowed for solution. The liquid was then poured into a large quantity of water, generally about fifty times the volume of the acid used, and the precipitated oxide collected, washed, and heated with hydrochloric acid, the chlorine evolved being estimated in the usual way by passing it into potassium iodide solution. As it was thought possible that not all the dioxide would be dissolved in the hydrochloric acid, but would remain suspended mechanically in the solution, and so give a too high result for the dioxide recovered, it was in several cases placed on a small filter, and hydrochloric acid allowed to drip on it slowly, the filtrate passing into a vessel of water, and being so precipi-

tated. The trace of tetrachloride remaining on the filter-paper was estimated separately and allowed for. By this method at 5° and −9°, from a specimen of dioxide containing 4·2 per cent. MnO, 54·2 per cent. and 53·8 per cent. were recovered. With a specimen of dioxide containing 72·1 per cent. MnO_2 and 12·5 per cent. MnO, 55·77 per cent. MnO_2 was recovered at 18°. At −20° this would correspond to the recovery of about 58·77 per cent. When some of this dioxide was shaken in a flask with hydrochloric acid and then poured into water, 56·49 per cent. was recovered; with hydrochloric acid saturated with chlorine, 56·54 per cent. was recovered, the temperature of solution being in both cases 18°. The reason of this slight increase lies probably in the fact that when hydrochloric acid is dropped slowly on to the dioxide on a filter-paper, the energy of the chemical action raises the temperature several degrees, and so more of the tetrachloride formed is decomposed.

With a specimen of dioxide containing 79·53 per cent. MnO_2 and 10·5 per cent. MnO, 55·5 per cent. was recovered at 13°. With a specimen containing 45·33 per cent. MnO_2 and 43·76 per cent. MnO, and consisting therefore mostly of Mn_2O_3, 74·5 per cent. MnO_2 was recovered, whilst with some Mn_3O_4, 85·43 per cent. was recovered. These last two experiments confirm Pickering's conclusions that the amount of dioxide recovered is largely increased if molecules of $MnCl_2$ be present in the solution.

It is thus seen that, instead of the amount of dioxide recovered being always slightly below fifty per cent., it is always slightly above it, if the solution be performed at ordinary temperatures. At the same time it is remarkable that it is not possible to recover by any means, except the introduction of $MnCl_2$ into the solution, a much larger proportion of dioxide than fifty per cent. The same explanation as was given before for this result, only more extended, may be used here. In the solution of manganese dioxide in hydrochloric acid at all temperatures, both low and high, it must be considered that the molecules of $MnCl_2$ and the atoms of chlorine are in a continuous state of recomposition together to form molecules of $MnCl_4$, and these are continuously decomposing again. At no temperature will the number of molecules of $MnCl_4$ actually existing as such in the solution, be much greater than half, unless, of course, additional molecules of $MnCl_2$ are present. On precipitation of the solution with water, therefore, only a little more than half the dioxide will be recovered, the atoms of chlorine present merely combining with one another to form molecules, which will dis-

solve in the water. The reason why the dioxide solution becomes much more stable with lowering of temperature is probably that the atoms of chlorine come the less often into the positions necessary for them in order that they may unite together to form molecules, although nearly as large a number of them may exist in the solution unattached to $MnCl_2$ molecules at the lower as at the higher temperature.

Even if slightly less than fifty per cent. of the dioxide were recovered on precipitation, this argument would still hold good, and so even in this case no proof would be afforded of the existence of the sesquichloride.

It has thus been shown that neither of Pickering's arguments can be held to prove that when manganese dioxide dissolves in hydrochloric acid, manganese sesquichloride, and not manganese tetrachloride, is formed; and as it has been shown in the former part of this paper that there is every probability that in the solution of the dioxide it is only the tetrachloride that is formed, we must consider that such is the case until stronger arguments than these have been brought forward to refute it.

Summary.

The chief conclusions arrived at in this paper are :—

(1) That when any of the oxides of manganese MnO_2, Mn_2O_3, and Mn_3O_4, are dissolved in hydrochloric acid, the only higher chloride formed is manganese tetrachloride, the equations for these reactions being :—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O;$$
$$Mn_2O_3 + 6HCl = MnCl_4 + MnCl_2 + 3H_2O;$$
$$Mn_3O_4 + 8HCl = MnCl_4 + 2MnCl_2 + 4H_2O.$$

(2) That this manganese tetrachloride solution is very much more stable at -26° C. than at ordinary temperatures, it being probable that at a still lower temperature it would undergo no decomposition whatever.

(3) That no evidence has yet been brought forward to show that any other higher chloride of manganese than the tetrachloride is capable of existence.

The University Laboratory, Oxford.

LX. *An Outline of* Mr. Mellard Reade's *Theory of the Origin of Mountain-Ranges by Sedimentary Loading and Cumulative Recurrent Expansion: in Answer to Recent Criticisms. By* T. Mellard Reade *.

Introduction.

IT is now four years since the 'Origin of Mountain-Ranges' was written, and during that time it has been subjected to considerable criticism by many able men in various parts of the Globe. I have purposely refrained hitherto from answering any of the objectors to my theory, feeling that it would be better to wait and weigh them. It appears to me now that most of the criticisms primarily spring from an imperfect realization of its principles, scope, and details.

The misconceptions no doubt largely arise from the complex nature of the problems and the difficulty of keeping the various threads of the argument unravelled. Under these circumstances, I have thought that the best reply I can make is to restate in a shorter manner the various salient points of my theory. Probably, if I had given the theory a name, and properly christened my bantling before sending it forth in the world to seek its fortunes, I might have been saved from paternal difficulties.

To prevent further misconceptions, I now name my theory the "Origin of Mountain-Ranges by Sedimentary Loading and Cumulative Recurrent Expansion."

The outline here given is of the barest character, and for illustrations, details, proofs, and quantitative calculations I refer those who want to know more to the work itself, as also for those portions which deal with other theories, and are of a destructive rather than constructive nature.

Condition of the Earth's Interior.

The Earth a Solid Spheroid.

The latest mathematical investigations go to prove that the Earth, taken as a whole, is solid, having a rigidity between that of glass and steel. The facts of physical geology are in accord with this view; for if the interior be wholly fluid, as some few contend, or if the nucleus be solid and the exterior shell solid with a zone of molten matter between, as others assume, the explanations of the physical conformation of the surface, its mountains and ocean-basins, become questions of flotation only.

The crust of the Earth would be like a sheet of ice. This

* Communicated by the Author.

fact seems to me never to have been fully realized by those theorists who favour either of these views.

The Nucleus of the Earth possesses a high Temperature.

There is such a general consensus of opinion that the earth at a depth of from 25 to 30 miles below the surface is at a temperature equal to that of molten rock at the surface that it is unnecessary for me to go over the arguments in favour of this widely prevalent view. If we assume that it is so, a very little calculation will show that matter at the depth of say 30 miles is subject to an enormous pressure, to which we can find no parallel by experimental methods at the surface. 30 miles = 158,400 feet; so that if we estimate that a column of the crust of the earth one inch square has a mean weight per foot of 1·5 pounds, the pressure at the depth of 30 miles will be in round numbers not less than 100 tons per square inch, or 14,400 tons per square foot. It has been proved by the experiments of the late Mr. Hopkins that there is in certain solids a relation between the melting-point and the pressure; so that, if the rock at the depth of 30 miles is at a temperature sufficient to melt it under ordinary pressures at the surface, the additional pressure of 100 tons per square inch may solidify it by raising its melting-point, or at least render it plastic. If the pressure increase more rapidly than the temperature as the earth is penetrated, what may be only semi-solid at 30 miles may become rigid at greater depths.

These points, from their nature, are incapable of direct demonstration, but possess a high degree of probability.

Shell of Greatest Mobility.

Although not accepting the hypothesis that there is a fluid zone under the Earth's crust, it would follow from the preceding considerations that the shell occupying the space between the solid rigid crust and the compressed rigid nucleus would respond to changes of pressure or temperature more readily than either the crust or the nucleus.

Facts of Physical Geology.

All great Mountain-Ranges are composed of great thicknesses of Sedimentary and other Deposits.

That all great mountain-ranges are composed of great thicknesses of sedimentary and volcanic deposits and igneous intrusions is a fact admitting of demonstration. It is true of the Alps, the Andes, the Himalayas *, the Rocky Mountains or North-

* Mr. C. S. Middlemiss, in his extended criticisms on the 'Origin of Mountain-Ranges' (Memoirs of the Geological Survey of India, vol. xxiv. part 2: Physical Geology of the Sub-Himalaya of Garhwál and Kumaun),

American Cordillera, the Appalachians, the Mountains of the Caucasus, and the Urals. The question at once arises in the mind, "Is this cause and effect?" If not, it is a coincidence somewhat in the nature of a miracle. If any one example to the contrary could be quoted, the argument of relation would be weakened, certainly not disposed of, but, so far as present knowledge extends, not one can be found.

Sedimentary Deposits out of which Mountain-Ranges have been built up extend over Vast Areas.

The deposits out of which great mountain-ranges have been elaborated by foldings, intrusions, and upheavals are not confined to the ranges and their immediate neighbourhood, but extend over vast areas. Speaking generally, modern geological investigation goes to prove that the thickest deposits lie, or have lain, towards the axes of the chains, though they may have been denuded from the actual axes*. Beyond the

calls in question this principle, though it is admitted by nearly all geologists since Dr. James Hall established the fact as regards the Appalachians in 1857. Quoting my words in the 'Origin,' "It is impossible to point to a range of mountains which has been built up of old denuded rocks," he completely misinterprets my meaning, which I had thought was plain enough from the whole tenor of the work. To give an illustration in the form of a prediction, I aver that no mountain-range will ever be built up out of any portion of the present land-area of Europe unless, and until, a basin of deposition has been established, and a thick sedimentary series deposited thereon. The old rocks may then be forced up along with the new, and form a constituent part of such a range. Unfortunately, as regards the Himalaya, information is meagre; but the granitic axes pointed to by Mr. Middlemiss as forming the highest peaks of the Himalaya are just what are required by my theory.

* Mr. Arthur Winslow, State Geologist of Missouri, in a paper just published in the 'Bulletin' of the Geological Society of America, entitled "The Geotectonic and Physiographic Geology of Western Arkansas" (vol. ii. pp. 225–242), has applied the principles enunciated in the 'Origin of Mountain-Ranges' to the explanation of an area in the Western part of the State tributary to the Arkansas River, 100 miles long in an East and West direction by 50 miles broad in a North and South direction. It is shown in an admirably concise and clear manner that the system of parallel interlocking anticlines and synclines having a general axial direction East and West is essentially Appalachian in character; that the Carboniferous strata of which they are composed increases in thickness from Missouri southwards into Arkansas; that the lateral movement has come from the South, and that the thickest strata are the most flexed. Mr. Winslow shows—a point that I have strongly insisted upon as characteristic of anticlines—that these geological features are elongated canoe-shaped domes having quaquaversal dips. He considers that the expansion of the lower layers of rock produced by the rising of the isogeotherms and their consequent protrusion in the form of anticlinal cores has fractured the apices of the arches, and thus exposed the upper layers

more folded and disturbed portions of the chain which often, so far as the newer sediments are concerned, lie on the flanks, the strata take on more gentle curvatures until, as in the case of the Urals, the Appalachians, and elsewhere where observable, they become nearly horizontal, or only have dips due principally to faulting.

The Tertiary and Cretaceous rocks extend from the Alps to the Caucasus and across the Mediterranean to the African coast, and may lie far beyond, as little is known of the geology of that part of the continent. They reappear in the Himalayas, and may be continuously connected, though this has not yet been proved. The same formations extend far to the eastward of the Rocky Mountains and the Andes, and most probably to the westward under the Pacific Ocean.

The greatest ranges of the world have been elaborated in Cretaceous or Tertiary times, and the connexion between sedimentation and upheaval is here most striking.

Sediments out of which Mountain-Ranges have been elaborated were laid down in Basins or Troughs formed by the bending of the Earth's Crust.

The thickness of the rocks, mostly conformable, composing some great mountain-ranges has been estimated by competent geologists at from 8 to 10 miles. The bulk of the rocks, as judged by their constitution, are usually considered by geologists to largely indicate either a moderate depth of water or actual shallow conditions. These rocks are intercalated with others exhibiting signs of a more oceanic origin. All the mountain-ranges mentioned may be pointed to in illustration of this statement. There is thus evidence that regional fluctuations of level in the Earth's crust have taken place on a large scale often succeeded by, as in the case of the Coal-measures, continued downward subsidence combined with shallow-water conditions.

It is evident, from these facts, that the great earth-troughs,

to energetic denudation. He infers also that the developed sections of such foldings are no measure of the original horizontal length of the beds —a principle I have strongly upheld, and which is being conceded by most geologists who have studied mountain-structure. The district seems to be one in which the first principles of the dynamics of mountain-building can be well analysed, as there is not such a complexity of causes to be considered and discounted as in the more colossal disturbances of the great mountain-ranges of the world. A few careful studies of mountain physiography such as this by geologists who have the opportunity and are equipped with the necessary physical knowledge would be of infinite service.

in which these materials for mountain-building were accumulated, were in some cases, on the final completion of sedimentation, double the depth of the deepest known oceanic troughs, which do not reach more than 5 miles.

Considering that there is a strong development of Cretaceous and Tertiary rocks extending along the western coast of North and South America, it is seen that these operations have there been carried on on an unusual scale. Deposit and alteration of level, elevation and subsidence, but preponderantly subsidence, progressed for an immense length of geological time in these areas, occupying not a mean portion of the Earth's history.

It is not, however, to be assumed that this was a continuous trough at any one time, rather that it consisted of a series of connected basins which underwent independent changes of level, the area being part of the time low-lying land interchanging with conditions of submergence.

Volcanic Action often Contemporaneous with the Laying-down of Materials for Mountain-Building.

Contemporaneous intrusive sheets of volcanic rock are a common occurrence in some part of the sedimentary history of a mountain-range. In addition, it is frequently found that volcanic ashes laid down in water, or subaerially, have a large development in rocks composing mountain-ranges; and necessarily, if these occur, dykes and volcanic rocks of the same age must exist in the foundation materials of the range.

Dynamical Principles.

Every theory which has hitherto been proposed to account for the elevation of mountains and the folding of the stratified beds forming the Earth's crust hinges finally on changes of temperature. Thus the tangential force generated in a rigid crust of low temperature by the cooling and shrinking of the Earth's nucleus has been invoked to account for the crumpling of the crust into mountain-ranges; the crumpled skin of a dried apple being the stock illustration. In this case, the force called in is *continuous* contraction by loss of heat. The theory which I have elaborated is one dependent upon *alternations* of temperature in the crust, contraction and expansion both being agents of uplift and lateral pressure.

Basins of Deposition and Loading of the Earth's Crust.

It has already been shown that the establishment of basins of deposition is the condition precedent to the building of a

mountain-range. There can be no deposition if there is not land-area enough either in the shape of continents, islands, or active volcanic orifices, or all combined or successive, to yield the necessary sediment. This furthermore implies considerable stability of conditions over lengthened periods of time combined with local mutations and changes of level, and, as I have indicated, we have the history of these mutations within the rocks of a range. The distribution of sediments is dependent upon the depth of the water surrounding the land and the currents of the sea (when they are not laid down in lakes or subaerially by rivers); but, whatever the conformation of the coast and sea-bottom, a continuous discharge of sediment upon it must in time load it, and, as proved by the enormous thickness of rocks composing great mountain-ranges, bend the crust below the maximum depth of any oceanic depression.

This necessary subsidence again insures the establishment of the basin of deposition and its continuous existence.

Displacement of Matter in the Shell of Greatest Mobility.

If the matter in a shell of the Earth between the nucleus and crust is in the condition I have postulated, it is evident that a lateral displacement of the matter of the shell must take place to some extent through weighting by sediment, and this will have its effect in raising the levels of the Earth's crust surrounding the basin of deposition; but will not be an agent in mountain-building.

Movement of the Isogeotherms.

It is evident, from the variations in the rate of increase of temperature that exist in various localities as the crust is penetrated, that the lines of equal temperature (isogeotherms) in the Earth's crust are subject to change, for it is not to be supposed that the temperature gradients have remained in their existing relations for all time.

It is also evident, as first shown by Babbage and Herschel, that the covering of any particular area of the Earth with sediment will necessarily raise the temperature of the crust below *. If, therefore, we assume a thickness of 10 miles of sediment to be laid down in a basin of deposition or earth-trough, and the rate of increase of temperature to be 1 in 50, what were originally surface-rocks possessing a surface-temperature determined by the climate of the locality will be

* This is well explained both by Babbage and Herschel in the 9th Bridgewater Treatise.

raised in temperature over 1000° Fahr., and eventually the whole of the underlying rocks of the earth's crust even below the shell of greatest change will be proportionately affected. The 10 miles of overlying sediments under such conditions would be raised 1000° Fahr. at the base, diminishing to zero at the surface.

Effects of the Rise of Temperature on the Foundation Rocks. Initial Stage.

The section of the crust of the Earth weighted and heated at the same time will be subjected to a gradually increasing compressive stress. So long as the actual expansive force of the heated crust is insufficient to raise the weight of sediment being piled upon it, it will continue to sink, though subject to vertical pulsations of level due to other causes, which it is not my object to treat of here. But there will eventually come a time when the accumulated stresses of the expanding rocks will overcome the weight of sediment, and then the upheaval, folding, and building of the mountain-chain will begin. But it is not to be supposed that the rise of temperature takes place with the mathematical precision described here for mere purposes of explanation *. I have shown that volcanic action often contributes to the foundation materials of a mountain-range, and that intrusive sheets and dykes penetrate the sediments, and ash-beds are laid down before the initial movement ushering in the birth of the range takes place. It is evident from this that there will be great variations of temperature taking place in the foundation crust and the sediments during their laying down.

The whole series of rocks, volcanic and sedimentary, will

* This seems a fruitful source of difficulty with some minds, beginning with Hopkins and ending with Hutton, Fisher, and Middlemiss. Their position seems to be this: if the rise of the isogeotherms into the new deposits eventually wrinkles and lifts them, why does it not begin at once? Why, for instance, should not 100 feet in thickness cause a rise, and if it does, how can thick beds ever be deposited? But there are thick beds, so the alleged *primum mobile* never acts. Q.E.D.

After making, as I fondly thought, full explanation of the *modus operandi*, I never anticipated the establishment of what a sense of humour compels me to call another *pons asinorum*. Even supposing the isogeotherms rose as rapidly as the deposits were laid down, the deposits could not be lifted until sufficient force accumulated to overcome the gravitation. But in a sinking area, as I have pointed out, if there be anything in the principle invoked, the presumption is that the isogeotherms are in process of sinking also, and it may take a lengthened period of sedimentation before they begin as a series to move upwards.

There are many other possible conditioning causes. A practical mechanical mind should soon see through this imaginary difficulty.

form a complex which will be simultaneously, but differentially, affected by the folding and elevation when that begins.

Unlocking the Igneous Forces of the Earth.

When once the elevation initiated only by piling-up of sediment, the sinking of the crust, and its consequent heating —otherwise by the rise of the isogeotherms—is established, a movement of the interior heated matter of the earth must take place towards the axis or axes of the range. This is proved by the frequency of granitic cores in great mountain-ranges, by the volcanic action accompanying their elevation, and its persistence or recurrence in a range even late on in its history, as instanced by the Andes, Rockies, and the mountains of the Caucasus, where volcanic cones surmount some of the highest granitic peaks, showing that these are the lines of least resistance through which the interior forces of the Earth expend themselves.

Heating of the Rocks of a Mountain-Range recurrent and constantly renewed during its History.

It is thus seen that the heated interior matter of the Earth is constantly being drawn towards and injected into the constituent framework of a mountain-range. When once the elevation of the sediments consolidated into rocky matter in the earth-trough begins through the influence of lateral pressure and the expanding mass beneath, a reduction of pressure and increase of volume takes place in the underlying fused rock. The compressive stresses of the rigid rock are partially relieved by folding and upward flow, and the temperature of the mass falls. Additional fused matter has been drawn from the interior, and in process of time the rocks of the range begin again to rise in temperature. Such fluctuations of temperature are well shown in the intermittent character of volcanic action. After a great outflow of lava, a volcano is quiescent sometimes for centuries. It has lost so much matter and so much heat, but the forces accumulate during the time of quiescence to burst forth with renewed vigour. Such intermittent activity I conceive is what takes place on a larger scale in the history of a mountain-range, but with greater time-intervals.

Dynamical Effect on the Strata of the Crust by Rise of Temperature.

The effect of a rise of temperature on the rocks of the Earth is, excepting in the case of unconsolidated clays, to increase

their bulk. From a great number of experiments made by me on sandstone, slate, limestone, and marble, I have estimated the coefficient of expansion of average rock at 2·75 feet lineal per mile for every rise of 100° Fahr.; but there is every reason to believe that the coefficient of expansion rises at higher temperatures than those at which my experiments were conducted. It has been urged by some of my critics that I have not allowed for the compression of the sediments filling the earth-trough into denser masses, but have credited all the expansion to mountain-building *. It has been overlooked that I have already explained that the weight of the mass alone will, by compressive extension, consolidate the beds below by reducing their thickness. Also the denser sedimentary rocks are often denser only by infiltration. This is particularly the case with sandstones, where the conversion into the final stage of quartzite is by the deposit of secondary silica in the interspaces of the grains, not by condensation.

Clays contract on heating; but, according to my views, the contraction of such beds in an earth-trough will be vertical only, by reason of the superimposed weight. A stage of metamorphism is at least arrived at, as we see in clay-slate, when the materials of that rock, originally clay, become metamorphosed so as to behave like other rocks, and expand with a rise of temperature.

Even if these criticisms possess much force, they do not apply to the rocky crust of the Earth already consolidated forming the earth-trough in which the sediments are laid down. There will be little or no loss by condensation in them, only straining or change of form. It is obvious that deep-seated rocks must be so compressed by simple gravitation, that lateral pressure will have little effect in further condensing them.

Recurrent Expansion Cumulative in its Effects.

If a given area of the crust of the Earth is raised in temperature, when the limit of elasticity is reached the surplus material must be disposed of by a change of form: it will rise in the line of least resistance.

Assume that the surplus due to the cubical expansion of a horizontal sheet is thrown into a ridge, and that then a fall of temperature takes place to the same extent. The material ridged up can never be drawn back again; it becomes a per-

* Hutton, Presidental Address, Section C, Melbourne Meeting of the Australasian Association for the Advancement of Science, p. 89.

manent feature of the Earth's surface. The contraction must be satisfied in another way, either by breaking up into blocks, faulting and subsidence extending through its substance, or by vertical contraction alone, and the lengthening of the beds by compressive extension due to the weight of superimposed materials. Probably both these principles generally come into operation together in nature. The Earth is bound to retain its solidity in whatever way that may be satisfied. If a rise of temperature then succeeds, the effect will be as before, and deformation will result, its locality being determined by the line of least resistance.

In the case of a mountain-range it will take place along or parallel to its axis, and the range will receive another accession of bulk.

Thus we see that the effect of alternation of temperature in the Earth's crust leading to the establishment of mountain-chains is cumulative. This cumulative effect of small alternations of temperature may be seen in the ridging-up of any old lead gutter, lead flat, or lead-lined bath or sink. It has been likened to a "rachet" movement, which is not an inapt illustration if taken with the necessary qualifications.

Effects of Contraction.—Normal Faulting.

Normal faults, that is faults that hade to the downthrow, are the result of contraction, and are posterior to the first plication. Any section of a mountain-range traversed by normal faults shows the folds sheared in a way that proves this. Normal faulting is, however, most prevalent in the less disturbed strata that flank a range. The mountain-range, pushed up by successive lateral thrusts or recurrent expansions acting over a great length of time and the folds thrown back and further compressed by the cores of gneiss and granite intruded into them, becomes a solid mass which cannot be drawn back by contraction. Contraction therefore has its maximum effect on the more horizontal deposits that flank the range, and extend for considerable distances on either side.

As the crust of the Earth must remain solid, the condition is satisfied by shearing and wedging-up by gravitation,—otherwise by normal faulting. Contraction of igneous masses beneath may induce this faulting in some cases, but it is not a necessary condition. Cubical contraction of the solid crust is sufficient.

Answers to some Objections.

The object of this outline of my theory is to focus its salient points, as many of my critics for some reason or other have failed to grasp them. What they criticise is frequently not my theory, but some rather vague notion called the "Herschel-Babbage" theory. What is exactly covered by this description I have a difficulty in ascertaining. On the other hand, one writer calls Mr. O. Fisher's theory, with which mine has no analogy, the "Herschel-Babbage" theory. I trust I shall give no offence by repudiating this labelling and claiming the theory as my own.

Neither Herschel, Scrope, nor Babbage ever advanced so far as to elaborate what could be justly called a theory of Mountain-Building. They gave to the world some fruitful suggestions, and acute reasoning thereon, which have been of considerable use to a succession of speculators in Geological Physics, and to myself among the rest*. One of the most frequently urged objections to my theory is the supposed inadequacy of expansion by rise of temperature to account for the excessive folding some mountain-chains have undergone, linear expansion only being considered. My reply to this is that even linear expansion alone places at our disposal more lateral movement than any other theory. It is true that those speculators who have invoked tangential thrust through the assumed shrinking of the Earth's nucleus, have had at their command any amount of lateral movement their imagination liked to draw upon, hence the simplicity and success of the theory—for a time. It has, however, been shown pretty clearly that the Bank upon which these cheques have been drawn is one of very limited liability†, and quite unequal to honouring them.

Prof. Hutton, in his very able address to Section C of the Melbourne Meeting of the Australasian Association for the Advancement of Science, gives an excellent *résumé* of the various hypotheses that have been suggested to account for Mountain-Building. I confidently appeal to his description to show that, omitting the theory of secular contraction of the Earth's nucleus, which he disposes of very effectually, none of the suggestions, theories, or hypotheses except the one I

* Until after my work was published I had read nothing of this but what was contained in Lyell's 'Principles' and letters, and Babbage's paper, read before the Geological Society in 1834, nor had I read Scrope's views.

† See Hutton's examination of this theory in the Address referred to.

support provides any lateral movement other than that due to intrusions of molten rock.

Prof. Hutton, in his description of my theory, doubtless given in the greatest good faith, leaves out what are in my view some of its vital and essential portions. I gave as an illustration the cubical expansion of an area of rock $500 \times 500 \times 20$ miles, and showed that it would, if raised 1000° Fahr., have an effective increase of bulk of 52,135 cubic miles *. Prof. Hutton seems to assume that this is the Alpha and Omega of my theory—the beginning and the end. I cannot but think it strange that he should take this view, as one of the first chapters† details illustrative experiments to give the reader the first conception of recurrent expansion.

The fact is, that there is no limit to the lateral movement provided by recurrent expansion, excepting the natural limit of the number and intensity of the successive changes of temperature.

I can assure Prof. Hutton that if I had advanced no further than the single constructive conception of cubical expansion as an agent in Mountain-Building, in itself original—or, at all events, not contained in the Herschel, Babbage, Scrope, or Lyell conceptions of the effects of expansion on the Earth's crust—the 'Origin of Mountain-Ranges' would never have been written.

Conclusion.

The object of this Outline being to correct some prevalent misconceptions of my views, I have confined myself principally to restating in a shorter form the essential principles of my theory of mountain-formation by sedimentary loading and cumulative recurrent expansion. For all the details, proofs, illustrations, and numerical calculations I must, as before stated, refer those interested to the original work. Perhaps it may lead some who have already read the 'Origin of Mountain-Ranges' to again read and reconsider it, when I trust the points I have touched on in this outline will add to its lucidity. Honest criticism, even if severe, is one means of elucidating the truth, and I not only invite but welcome it.

Park Corner, Blundellsands,
Liverpool.

* 'Origin of Mountain-Ranges,' p. 116.
† *Ibid.* Chap. III.

LXI. *Allotropic Silver.*—Part III. *Blue Silver, soluble and insoluble forms.* *By* M. Carey Lea*.

WHEN my first paper on the subject of allotropic silver was published about two years ago, that product seemed to be the result of a very limited number of reactions closely allied to one another. Further study has shown that it is a much more common product than at first appeared to be the case. Wherever in the reduction of silver a reddish colour shows itself, that may be taken as a probable indication that allotropic silver has been formed, even although it may be destroyed before it can be isolated.

What is rather remarkable, is that allotropic silver is produced abundantly in certain very familiar reactions in which its presence has never been suspected: so abundantly, in fact, that some of these reactions constitute the best methods of obtaining silver in the soluble form. In photographic operations silver has often been reduced by tannin in the presence of alkalies. It has not been imagined that by slightly varying the conditions, the whole of the silver may be made to pass into solution as a soluble metal with its characteristic intense blood-red colour.

Some of these new reactions will be here described in detail.

Allotropic Silver formed by Dextrine and Alkaline Hydroxide.

When dextrine is dissolved in a solution of potassium or sodium hydroxide, and silver nitrate is added, keeping the hydroxide in moderate excess, the silver is at first thrown down in the form of the well-known brown oxide. This brown colour presently changes to a reddish-chocolate shade, and at the same time the silver begins to dissolve. In a few minutes the whole has dissolved to a deep-red colour, so intense as to be almost black. A few drops poured into water give it a splendid red colour of perfect transparency. Examination with the spectroscope leaves no doubt that we have to do with a true solution.

It is interesting to observe that silver can be held in solution in neutral, acid, and alkaline liquids. In the first process which I published, in which silver citrate is reduced by a mixture of sodic citrate and ferrous sulphate, the latter may be used either in acid solution, or it may be first neutralized with alkaline hydroxide, so that that form of silver is held in solution in either a neutral or an acid liquid. The form that

* Communicated by the Author.

is obtained with the aid of dextrine dissolves most freely in the strongly alkaline liquid in which it is produced, and when dilute nitric or sulphuric acid is added, the silver is precipitated. But with acetic acid the precipitation is very incomplete: the solution retains a brown colour, and contains silver. Even the addition of a large excess of strong acetic acid fails to throw down any more silver. It follows, therefore, that whilst this form of silver is most freely soluble in a strongly alkaline liquid it is also soluble, to some extent, in one that is either neutral or acid.

The precipitate, when once formed, appears to be almost insoluble. A small portion of it stirred up with distilled water gives no indication of solution. But if a quantity is thrown on a filter and washed, as soon as the mother-water is washed out, the liquid runs through of a muddy red; and if this filtrate be allowed to stand, it deposits an insoluble portion, and then has a fine rose-red colour and perfect transparency. Notwithstanding the beautiful colour, it contains a trace of silver only, so great is the colouring-power of the metal. Sometimes, if the alkaline solution stands for a month or two, the silver becomes spontaneously insoluble; most of it falls to the bottom as a deep-red substance, but part remains in suspension, with a bright brick-red colour. The difference between this and the true solution as originally formed is extremely well marked.

Dextrine is a very variable substance, and different specimens act very differently. Common brown dextrine seems to do better than the purified forms.

Convenient proportions are as follows:—In 2 litres of water 40 grammes of sodium hydroxide may be dissolved and an equal quantity of dextrine, filtering if necessary. 28 grammes of silver nitrate are to be dissolved in a small quantity of water, and added by degrees at intervals. Complete solution readily takes place. Although the liquid contains less than 1 per cent. of metallic silver, it appears absolutely black, when diluted red, by great dilution yellowish. With some specimens of dextrine the solution remains clear; with others it soon becomes a little turbid.

Perhaps the most interesting reaction which this solution shows is that with disodic phosphate. A little phosphate is sufficient to throw down the whole of the silver, although both solutions are alkaline. When a gramme of phosphate in solution is added to 100 cub. centim. of silver solution, the colour becomes bright red, sometimes scarlet, and the whole of the silver is presently precipitated. This precipitate on the filter has a colour like that of ruby copper, which colour it retains during the first washing; but after a few hours' washing with

distilled water, the colour changes to a deep Nile-green, and at the same time it becomes slightly soluble, giving a port-wine coloured solution. With more washing, this solubility may disappear.

It is a general fact that all these forms of silver, however various their colour, have both a body- and a surface-colour; and these two colours tend always to be complementary. The body-colour is that shown by the precipitate while still moist; it is also visible when a thin coat is brushed over paper, a coat so thin that light passes through it, is reflected by the paper, and returned again through the film. But when a thick and opaque film is applied, the body-colour disappears, and only the complementary surface-colour is visible.

So in the case of the precipitate by phosphate, when the substance resembling ruby copper is spread thickly on paper, it dries with a bright-green metallic surface-colour. But when the substance itself becomes green by continued washing, it assumes, on drying, a dark gold or copper colour, the surface-colour changing with the body-colour and maintaining its complementary relation. In observing these effects one is constantly reminded of certain coal-tar colours, both by the great intensity of coloration and by the metallic surface-colour. I am not aware that any other inorganic substance shows this resemblance to a similar extent.

These forms of allotropic silver have a great tendency to attach to themselves foreign matters. Although the dry substance has all the appearance of a pure metal, it may contain as much as 8 or 10 per cent. of organic matter, which it is utterly impossible to detach. I have taken much trouble to eliminate this substance. In one attempt hot distilled water was forced through with the aid of a filter-pump for over one hundred hours, without effect. The presence of this organic substance becomes evident when the metal is heated in a tube. A vapour arises which condenses into small brownish drops having an empyreumatic odour. The residue of bright white metallic silver, when dissolved in nitric acid, leaves behind black flakes of carbon. When the allotropic silver is dissolved in dilute nitric acid and the silver precipitated by hydrochloric acid, on evaporation a small residue of a yellowish gummy substance is obtained.

Analyses.—Four silver determinations were made of material rendered as pure as it was found possible to obtain it. Results:—

No. 1	.....	93·77 per cent.	Ag.
„ 2	.....	94·27 „	„
„ 3	.....	92·86 „	„
„ 4	.....	96·64 „	„

Allotropic Silver obtained with Tannin and Alkaline Carbonates.

Tannin (gallotannic acid) in alkaline solution reduces silver nitrate to metallic silver in the allotropic form. Tannin acts more strongly than dextrine, and therefore does best with carbonated alkali, dextrine best with alkaline hydroxide, although either substance will produce the reaction with either form of alkali and, though less advantageously, with ammonia. Tannin with sodium carbonate gives a very perfect solution of silver, quite free from the turbidity that is apt to characterize the dextrine solution. The colour of this solution is likewise very intense: one containing 1 per cent. of silver is quite black, on dilution deep yellowish red. It has very much the same characters as the preceding, but is rather more stable. To obtain it, 24 grammes of dry sodium carbonate may be dissolved in 1200 cub. centim. of water. A 4-per-cent. solution of tannin is to be made and filtered; of this, 72 cub. centim. are to be added to the solution just named: of silver nitrate, 24 grammes dissolved in a little water are to be added by degrees. Solution takes place almost instantly as each successive portion is added. The solution, after standing a day or two, may be decanted or filtered from a small quantity of black precipitate.

When the solution is treated with a very dilute acid, as, for example, nitric acid diluted with twenty times its bulk of water, allotropic silver is precipitated in the solid form. It dries with a brilliant metallic surface-colour of a shade different from the foregoing, and somewhat difficult to exactly characterize, a sort of bluish steel-grey.

I do not find that the blue allotropic silver (in which is included the green and steel-grey varieties) can be reduced to any one definite type. On the contrary, its variations are endless. Slight differences in the conditions under which the solutions are formed, or in the mode of precipitation, give quite different products. For example: of ten products obtained with tannin and sodium carbonate in different proportions, several were easily and completely soluble in ammonia, some were slightly soluble, and some not at all. Some specimens not at all soluble in water became so by moistening with dilute phosphoric acid: they did not dissolve in the acid, but when it was removed they had become soluble in water. On other specimens phosphoric acid had no such effect. Some solutions are scarcely affected by acetic acid, others are partly precipitated, others almost, but not quite, wholly. The films

spread on paper vary very much in their relations to light; some are readily converted into the yellow intermediate form, whilst others are very insensitive. The least sensitive specimens seemed to be those for which dilute nitric acid had been used as a precipitant: they had a steel-grey colour. Precipitation by acetic acid seems to tend to a greenish metallic surface, colour, and greater sensitiveness. Different specimens also vary very much as to permanency; this character is also affected by the amount of washing received: thorough washing tends to permanency.

In some way the blue, grey, and green forms seem more closely related to the black or dark grey forms of normal silver, for they tend, in time, to pass into them; whilst, on the contrary, gold-coloured silver, if pure, tends, with time, to change to bright white normal silver on the surface with dark, or even black, silver underneath.

Action of other Carbonates.

Tannin is capable of producing allotropic silver, not only in the presence of the carbonates of potassium and sodium, but also with those of lithium and ammonium, and also with the carbonates of calcium, magnesium, barium, and strontium. The action of the last-named carbonate has been more particularly examined. It yields allotropic silver of a dark-red colour whilst moist, drying with a rich bluish-green metallic surface-colour in thick films, in very thin films transparent red. It is probable that the substances with which tannin produces these reactions would be further increased by investigation.

I have found some additional modes of production of these forms of silver, modes which are very curious and interesting. They are now being studied, and will be reported on hereafter.

Nature of the "Intermediate Substance."

It has been mentioned in previous papers that when allotropic silver is converted into normal silver by the action of heat, it passes through a perfectly well-marked intermediate state. In this state it retains the gold-yellow colour and high lustre, but none of the other properties of the original form. Oxidizing and chlorizing agents show nearly the same indifference as with ordinary silver. Whilst allotropic silver is soft and easily reduced to powder, the intermediate substance is hard and tough. When a glass rod is drawn over a film of allotropic silver, it leaves behind it a white trace of ordinary silver. The intermediate substance shows no such

reaction: the trace of a glass rod does not differ from the rest of the film; and even hard burnishing produces no change in the colour. Continued exposure to sunlight brings about the same alteration to the intermediate form, and it takes place spontaneously with time.

At that time no explanation could be found as to the nature of the change. It proves, however, to be a passage into a crystalline form. Some films spread on paper were exposed to the action of very dilute solution of ferric chloride. It chanced that one of these films had undergone a partial change into the intermediate form; the unchanged portion was darkened by the ferric solution, whilst the portion that had passed into the intermediate form retained its bright gold-yellow colour and lustre, rendering it thus distinguishable. The figures which it exhibited were strikingly crystalline. One portion showed a foliated structure, such as is formed by interpenetrating crystals; other parts showed ramifications with something of a plant-like form. Another part exhibited a sheaf of acicular crystals nearly parallel in direction half an inch to an inch long, and as fine as hairs. These appearances indicated with certainty crystalline structure. Other specimens have been obtained, though none so well defined as that just mentioned, which happened to be taken at exactly the right stage of spontaneous alteration to make the structure manifest. The alteration is not apparent to the eye, as the colour does not change.

This change to the crystalline condition does not seem to be peculiar to gold-coloured silver. The blue form, when gently heated in a tube, becomes yellow. By continued heat it changes to white normal silver. A film on glass began to change from blue to yellow at about 180° C. Light also produces this change on blue silver. The specimens obtained by different processes act very differently; some change with a few hours of strong sunlight, others require many days.

From what has been written in this and preceding papers, it appears that allotropic and even soluble silver may be formed in a great variety of reactions. The reducing agent may be either a ferrous or a stannous salt, or any one of a variety of organic substances of very different constitutions. From the solubility and activity of this substance and the parallelism which many of its reactions show to those of silver in combination, I have been disposed to think that silver in solution might, like silver in combination, exist in the atomic form. It is certain that, up to the present time, we have no

positive knowledge of the existence of any element in the atomic form as a solid. We know that four or five metals are atomic in their vapours, and that in iodine vapour at a certain temperature the molecules separate into atoms.

But it may be questioned whether we have not seen solid elements in the atomic form without recognizing them as such. There are forms of iron, nickel, cobalt, and lead which exhibit very remarkable properties, properties that have been hitherto very unsatisfactorily explained. Lead tartrate reduced by gentle ignition in a nearly closed tube, and allowed to cool and then shaken out into the air, forms a stream of fire. The oxides of iron, nickel, and cobalt reduced in closed tubes by hydrogen show similar properties. It is customary to explain this action by affirming that the metals are left in an extremely fine state of division. This explanation is not satisfactory. Sulphur, for example, is far more inflammable than any of the metals just mentioned, and may be obtained in a state of exceedingly fine division, either by sublimation or by precipitation; but does not, in consequence, show any greater tendency to spontaneous inflammation. It seems more natural to suppose that these metals are reduced in the atomic form; and this view of the matter seems to be much strengthened by the following considerations.

The experiments of Ramsey and of Heycock and Neville, cited in a previous paper, lead to the conclusion that in the case of a dilute solution of one metal in another the dissolved metal exists in the atomic form. But still more, the experiments of Tammann on amalgams indicate that in these alloys the dissolved metal is atomic; and it is stated that Joule, by distilling off the mercury from an iron amalgam, found that the iron was left in a pyrophoric condition. The amalgam of manganese, carefully distilled, gives a pyrophoric powder. Chromium amalgam, distilled in a current of hydrogen, gives a similar result if the temperature is not raised too high. The enormous affinity which these forms of metals exhibit for oxygen renders their study very difficult. It has not been before suggested that their activity is due to their being atomic; but this would seem to be a much more rational explanation than that of extreme division*. A broad distinction must of course be drawn between chemical and mechanical division: a substance may be atomic and yet appear in masses; may be in the finest mechanical division and yet be molecular

* M. G. Rousseau, in the new *Encyclopédie Chimique*, seems to entirely abandon the old view of extreme division, and considers these forms to be allotropic, and comparable with the allotropic forms of phosphorus, &c., Vol. iii. p. 56.

or polymerized. Silver being a metal with a very low affinity for oxygen, could not be expected to show in the atomic state the same inflammability as more oxidable metals.

In conclusion, it may be said that there is much reason to suppose that elements may exist in the atomic form, and that allotropic silver may present such a case. This is, of course, far from being proved, and is offered only as a "working hypothesis." As such, it may afford a useful aid in further investigations.

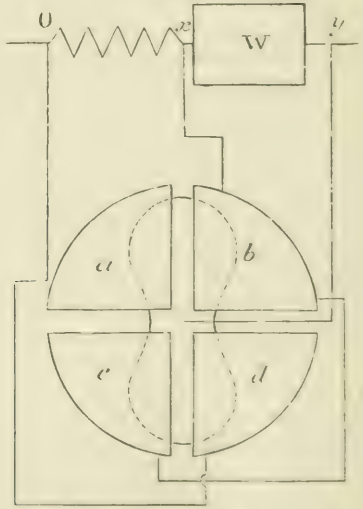
Philadelphia, April, 1891.

LXII. *The Electrometer as a Wattmeter.* *By* J. Swinburne *.

IN 1881, when M. Joubert published his experiments on a Siemens machine, in the course of which he had used a Thomson or Mascart electrometer as a voltmeter, Professors Ayrton and Fitzgerald simultaneously proposed to use the quadrant electrometer as a wattmeter.

The ordinary method of arranging the instrument is shown in fig. 1. The resistance is wound so as to be non-inductive :

Fig. 1.



and the power to be measured is spent in the apparatus marked W. If the fall of potential between x and y is very great in comparison with that over the resistance, the instrument reads like a charged electrometer, and it may be taken to read in watts. In practice such conditions do not occur ;

* Communicated by the Physical Society : read March 6, 1891.

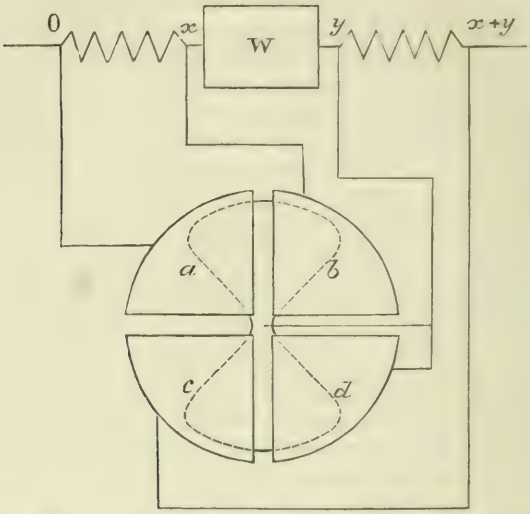
for if the resistance is made low the instrument is not sensitive enough, and if it is made high the electrometer no longer reads in watts. If the instantaneous pressures are 0, x, and y, the force exercised by the first quadrant a in the positive direction is $k\ y^2$, where k is the constant of the instrument. This constant may be omitted, and the force denoted by y^2. The force exercised by b is $-(y-x)^2$; by c, $-(y-x)^2$; and by d, y^2. The total force is thus $2\ (2y-x)\ x$. The needle contact may now be moved from y to x and another reading taken. This is of course $2\ x^2$. Subtracting this from the first reading, we get $4\ (y-x)\ x$, which is the power taken by W. This is the arrangement that was adopted by Dr. Hopkinson in his measurements of the Gaulard and Gibbs transformer in 1884. During the first reading the instrument is really two idiostatic voltmeters, one being in shunt to both the resistance and W, and the other in shunt to W alone. During the second reading it is a voltmeter in shunt to the resistance alone.

Professor Ayrton arranges the instrument so that the quadrants are in shunt to W, and the needle is first connected to x and a reading taken, and the needle is then connected to 0 and a second reading taken. During the first reading, the instrument is a voltmeter in shunt to W, and during the second it is two voltmeters, one in shunt to the resistance and one in shunt to the whole circuit. The difference again gives the power spent in W. Mr. Smith uses a discharge-key for making a change quickly. The discharge-key can be used in either arrangement, but the first is more accurate. For instance, suppose $y-x$, the pressure on W, is 2000 volts, and x, the pressure on the resistance, 20, and suppose the instrument one per cent. low at one reading. The first reading by the second method is 8,000,000, the second 8,160,000. Suppose the latter is read one per cent. low, viz. 8,078,400, the resulting determination is 78,400 instead of 160,000 ; that is to say, the power is more than 100 per cent. greater than that given by the instrument. In the arrangement used by Dr. Hopkinson, however, the readings are 160,800 and 800, so a misreading of one per cent. in the first makes one per cent. error only, and in the second makes no sensible difference.

The quadrant electrometer may, however, be arranged so as to read power directly without any change of connexions. This is shown in fig. 2. A second resistance equal to the first is put on the other side of W, and the quadrants are connected up as shown. The first quadrant a then has a force y^2, the second b, $-(y-x)^2$. So far the instrument is like that shown in fig. 1, but with only half its quadrant utilized. Quadrant c has a force $-x^2$, and d is inactive ; so that quadrant c

makes the correction for which the second reading was necessary in fig. 1, so the instrument can be graduated in watts.

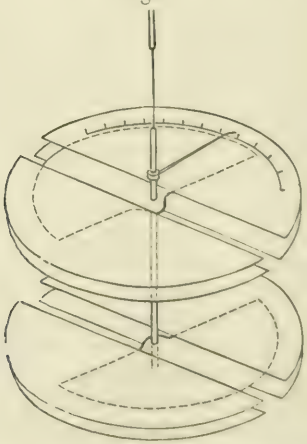
Fig. 2.



There may be some slight error due to the whole needle being drawn into the quadrants *a* and *b*, and out of *c* and *d*. This is obviated by making the needle of such a shape that there is no appreciable end pull, as shown in fig. 2.

Fig. 3 shows a form for a direct-reading instrument with

Fig. 3.



a pointer or index. Instead of quadrants it has half-disks, like the Blondlot and Curie electrometer, but, unlike it, this

form has four pairs of half-disks. The Blondlot and Curie form also reads power directly, but the needle is made in two insulated portions, and needs two metallic connexions, and this gives rise to mechanical troubles and loss of sensitiveness. The instrument shown in fig. 3 has the needle all in one piece, and the disks can be so far apart that errors from variations of height of the needle due to variations of the length of the fibre do not become serious. A long suspension of phosphor-bronze wire is, however, preferable for most purposes.

LXIII. *Alternating and Experimental Influence-Machine.* By Mr. James Wimshurst, *Member of Council**.

I HAVE pleasure in bringing to your notice a new form of influence-machine which is self-exciting, notwithstanding that when at work its electrical charges alternate during each revolution.

In order that you may readily follow the action of the machine when at work I will first describe its construction in all its details.

It consists of a base or frame, from the sides of which rise the standards to carry the spindle and boss for the rotating disk, suitable driving gear being fixed thereto.

In the same plane as the rotating disk is fixed a square wooden frame having the necessary holes, plugs, and clamps, by means of which the inductor-plates are held in position.

The rotating disks are cut from ordinary window glass, and are coated with shellac ; they are 16 inches in diameter ; one of them has no metal upon it, the next has four medium-sized tin-foil sectors upon each of its sides, the last of this series has 16 sectors upon each side ; other disks have from 2 to 4 sectors of large size upon them ; another disk has four large sectors upon each side, so placed that the sectors upon one side cover those upon the other side ; another has four very narrow sectors upon each side, and another has 16 sectors all upon the one side.

The inductor-plates are squares of glass measuring $9\frac{3}{4}$ inches; one corner of the plate is cut away to admit the spindle and the boss. They are coated with shellac, and upon one side of each of them is a tin-foil patch, and a suitable device for holding the rod and the brush.

Two of these inductor-plates are mounted at the diagonal corners, upon one side of the wooden frame, and two upon the other side of the frame ; those at the front of the machine are at the lower right-hand corner and the upper left-hand corner ; those at the back of the machine are at the upper right-hand

* Communicated by the Physical Society : read April 17, 1891.

corner and the lower left-hand corner: the rotating disk is therefore covered for one half of its surface upon both of its sides.

The brushes are made of fine brass wire, and the brush-holders are brass rods, bent to a form to admit of the brushes touching the rotating disk at a point opposite to the middle of the next following induction-plate: this arrangement supplies two brushes to each side of the disk, and the brushes when in place are situated 180° asunder.

The several parts of the machine are interchangeable, and by means of the varied combinations many experiments can be made; in fact its combinations include nearly every type of electrical influence-machine.

The prominent results obtained from it are:—(1) That glass disks which have no metal upon them are freely self-exciting. (2) That the freedom to self-excitement increases about proportionally to the number of sectors. (3) That the quantity of electricity decreases with the amount of metal upon the disk—whether the amount be in the greater number of sectors, or the increased size of sector (chiefly the latter).

The only tests as to when the alternations occur which I have been able to make were made by means of a sensitive arrangement of light paper disks, suspended by fine wire. When this apparatus is connected to one of the inductors, and the glass disk turned very slowly, the alternations are seen to occur with each $\frac{3}{4}$ revolution of the disk; when the disk is turned much faster, then the alternations occur too rapidly for the paper disks to respond, and they hang motionless and nearly together.

It is not possible to obtain any sensible charge in a Leyden jar, although the electricity may be clearly seen as a stream between the jar and the inductor.

Another series of combinations may be made by removing the two inductor-plates from the back of the machine and substituting an insulating arm extending across the disk, it having wire brushes at its ends, the brushes being connected metallically with terminal balls. When this combination is in use the charges no longer alternate unless the terminal balls are separated beyond the sparking distance. The plain glass disk without metal sectors, and also the disks having large sectors upon them, are no longer self-exciting. The glass disk having 16 sectors upon one side is not self-exciting when placed so that the sectors touch the brushes of the inductors, but when placed so that the sectors touch the brushes of the insulating arm it then becomes freely self-exciting. All disks having medium-sized sectors upon each side are freely self-exciting.

I have noted many of these results in tabular form.

Table showing Results of Combinations.

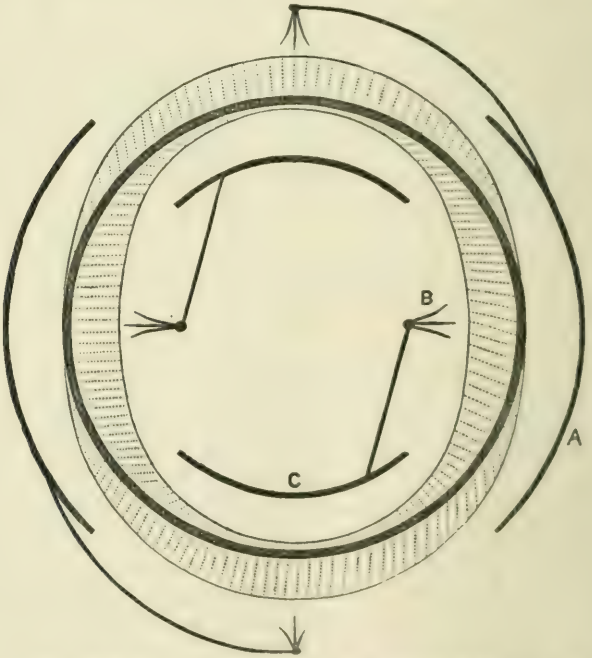
Disks.	Four Large Inductors.	Four Small Inductors.	Two Inductors and Rod.
Plain glass and no metal.	Is self-exciting with about 4 revolutions. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting but requires care. Alternations occur each $\frac{3}{4}$ revolution.	Is not self-exciting but requires little assistance. Constant current while not overtaxed; gives large current.
Two metal sectors each side.	Is self-exciting. Alternations occur after each two sectors pass brush.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Constant current.
Four metal sectors each side.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Constant, but gives less current.
Eight metal sectors each side.	Is more freely self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Constant current.
Sixteen metal sectors each side.	Is freely self-exciting with 3 revolutions. Alternations occur each $\frac{3}{4}$ revolution.	Is more freely self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is freely self-exciting. Constant, but gives less current.
Sixteen sectors on one side.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting. Alternations occur each $\frac{3}{4}$ revolution.	Is self-exciting when sectors are next the rod. Is not self-exciting when sectors are next inductors. Constant in either case.

NOTE.—The principal features are:—1. That glass disks with no metal upon them are capable of self-excitement. 2. That the self-excitement increases about proportionally to the increase in the number of sectors. 3. That the quantity of electricity decreases about proportionally to size of sectors and also their number.

I now feel uncertain as to whether I should end my paper at this stage, or whether I should extend it into the region of opinion. If I remain silent I am sure the cause of the electrical action will be dealt with by abler minds than my own. On the other hand, I feel equally sure that many will wish me to indicate a working hypothesis ; therefore, and by way of suggestion, I will add what seems to me to be a reasonable explanation.

As to the initial charge, I think it may be accepted that all bodies behave as though they possessed a film of electricity over their surfaces, and that when two or more of these bodies are brought together this normal electrical condition is upset, for the electricity which was upon their near surfaces is repelled to the outer or bounding surface—it is this excess charge upon the bounding surface, minute it may be, which constitutes the first charge.

In respect to the electrical action which takes place in this particular machine, I will endeavour by the help of the small diagram to explain.



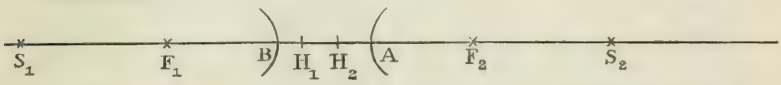
Assuming that we have obtained an initial charge and that it is brought to the inductor marked A, then, neglecting the changes which take place between the two bounding surfaces,

we obtain by induction an excess of electricity upon the far surface B of the rotating disk: this excess in its turn is conveyed by the brush and its holder to the next inductor C, which in its turn repeats the operation, and so on with each inductor, for the inductors are, as you see, situated alternately, the first upon one side, and the next upon the other side of the rotating disk. These excesses of electricity seated upon the rotating disk, opposite to the inductors, may be viewed as wave-crests, while the corresponding depressions are under the surface of the inductor. All that is done by the machine is to produce this wave-action in the electrical coating or film; for there is no metallic connexion between inductor and inductor, nor between the machine and the earth: moreover, all the inductors are charged with electricity of one sign, although, probably, the potential in one inductor may be slightly different to that in the other.

The alternations are possibly caused by the repulsion between the electrical charges upon the disk and the inductor, and the consequent slipping of the electrical film upon the inductor in such manner as to produce a break in the phase of the wave in relation to the brushes.

LXIV. *The Focometry of Diverging Lens-Combinations.* *By* Professor A. Anderson, *M.A.**

On reading the abstract of a paper by Prof. S. P. Thompson, "On the Focometry of Lenses and Lens-Combinations, and on a new Focometer," in the 'Proceedings of the Royal Society,' vol. xlix., no. 298, it occurred to me that the same principles are applicable to the case of diverging, or positive, combinations, and that the method might be modified so as to make it capable of measuring the focal lengths and finding the positions of the principal points of such combinations.



Let light be incident from right to left on the surface A at a small distance from its vertex, the direction of the light being inclined at a small angle to the axis, and let F_1 and F_2 be the principal foci. Then, distances being measured to the right from H_1 and H_2, the principal points, we have the ordinary formula

$$\frac{1}{v} - \frac{1}{u} = \frac{1}{f}.$$

* Communicated by the Author.

Hence, if $u=-2f$, $v=2f$; or, if light converge to a point S_1 such that $H_1S_1=2f$, it will, after passing through the combination, diverge from S_2, where $H_2S_2=2f$. S_1 and S_2 are the symmetric points, and it is clear that $S_1F_1=F_2S_2=f$.

The combination A B should be fixed on a support which is capable of a lateral motion at right angles to the length of the optical bench, so that the axis of the combination may be placed in or out of the axial plane of the bench at pleasure. The additional parts required are two supports which can slide along the bench, each furnished with a convex lens and cross wires. The line joining the intersections of the cross wires should be parallel to the bench and coincident with the axes of the lenses and that of the combination when in the axial plane. The lenses should be of exactly the same focal length, and the cross wires of both should be placed outside (or away from the combination) at equal distances, greater than this focal length, from the lenses. It would be an advantage if the positions of the cross wires could be altered relatively to the lenses, but in making a measurement they should be at equal distances from them.

Suppose, now, the focal length of a diverging combination has to be measured. A telescope furnished with cross wires, and which has been focused for parallel rays, is used to view the cross wires of one support through the convex lens of that support and the combination, the support being moved along the bench till the cross wires are seen without parallax. The combination is then moved out of the axial plane, and the position of the image of the cross wires formed by the rays passing through the convex lens observed. This gives one of the focal points, and the position of the other can be found in the same way, using the other sliding support. Transparent micrometers may now be placed at these points, as in Prof. Thompson's method. The two supports are then placed so that their cross wires are at equal distances from the micrometers, and moved along the bench through equal distances in opposite directions till the image of the cross wires of one support coincides with the cross wires of the other, the combination having of course been previously moved back into the axial plane. The combination is then again moved out of the axial plane, and the micrometers are moved till the images of the cross wires are seen in them. The distance moved through by either is the focal length of the combination.

It should, if necessary, be possible to remove the convex lenses and replace them by others more suitable for the actual combination to be measured. Of course the apparatus with-

out the sliding supports may be used for finding the focal length and principal points of a convex combination.

It would, no doubt, be easy to construct the apparatus so that the same screw could move both the pair of sliding supports and the pair of micrometers independently. But it seems a simpler method, after first finding the principal foci, to obtain with only one of the convex lenses an image of its cross wires on a suitably placed screen, by rays passing through both the lens and the combination. The position of the conjugate focus of this image can then be found by moving the combination out of the axial plane and obtaining the image of the cross wires formed by rays passing through the convex lens alone. The distances of these conjugate points from the principal foci are then measured, and the focal length is given by the formula $dd'=f^2$.

A support of the kind described above, furnished with a convex lens and cross wires, would be required in many cases for determining the focal or symmetric points of positive or negative systems; but in no case would a knowledge of the focal length of the lens or any calculation involving it be necessary.

LXV. *Notices respecting New Books.*

Higher Geometry, containing an Introduction to Modern Geometry and Elementary Geometrical Conics. By W. J. Macdonald. (Edinburgh: J. Thin; 184 pp.) (i.)

Supplement to "Euclid revised," being an Introduction (within the limits of Euclidian Geometry) to the Lemoine and Brocard Points, Lines, and Circles. By R. C. J. Nixon. (Oxford: Clarendon Press; pp. 378–426.) (ii.)

Pitt Press Euclid, iii.–iv. *By* H. M. Taylor. (pp. 167–326.) (iii.)

Geometrical Deductions. Book I. *By* J. Blaikie *and* W. Thomson. (London: Longmans; pp. viii + 138.) (iv.)

WE have grouped these elementary geometrical Text-books together and briefly indicate their contents.

(i.) is a short course which the author has used in his own classes for many years, so that it represents what an experienced teacher has found suitable for junior pupils. It deals with the fundamental theorems of Harmonic pencils and "Cross Ratios" in a clear manner, and after a brief look at Linkages introduces the student to the simpler properties of the Conic Sections. The book furnishes a good introduction to Housel, Dr. C. Taylor, and other writers on the subject.

(ii.) is an account, of the Circles and Lines discussed, with proofs that must satisfy the most rigid adherent of Euclidian methods. This little pamphlet will do much, we feel sure, to make this

modern or *surname* Geometry acceptable to English students. On p. 385 there is a too general statement which requires correction (see first five lines).

(iii.) We like this second instalment of the Elements better even than we liked the previous one. Mr. Taylor's treatment in parts differs from that of other writers, there being a good deal of rearrangement in the first twelve propositions, but the matter treated of agrees in substance with that given in Euclid's first twelve propositions. Ptolemy's theorem (the so-called Euc. vi. D) comes in as Prop. 37 B, being prefaced by Prop. 37 A. There is also an interesting additional proposition which involves the principle of the rotation of a plane figure about a point in its plane. There are also some propositions on Poles and Polars, on Radical Axes, on Orthogonal Circles, and on the Nine-point Circle of a Triangle. The carefully selected examples are a valuable feature of a good elementary edition of the 'Elements.'

(iv.) The idea of this capital little book of Riders is: "first a deduction is worked out in full, which is intended to serve as a model for the student. This is followed by a number of similar deductions, which are to be written out by the student, the figure being given in each case, and such hints regarding the mode of solution as experience shows are required by beginners. Lastly, each section contains some deductions to be accomplished without this aid, no figures or assistance being given except an occasional reference to the proposition on which the proof depends, or to a previous example." It will be thus seen that the idea is an excellent one for the majority of young students, and it is very well carried out. The abundance of good figures is a strong feature. After working through all the exercises we can strongly recommend the book, the only drawback that we see being that few can give so much time to the thorough getting up *one* book of the Elements as is involved in working out all the deductions. The student, or his teacher for him, must make a selection if he has not time. This we think we can guarantee, that when he has worked through this collection, he will make short work of the major part of the deductions which he will meet with in ordinary school examinations.

Die Elektrischen Verbrauchsmesser—Electricity Meters. *By* ETIENNE DE FODOR. (Leipzig: A. Hartleben.)

THE series of which the present volume forms a part contains some excellent treatises on various subjects connected with electrotechnics written by competent continental specialists. It is greatly to be regretted that they are not accessible to the majority of English readers on account of their being written in German. So far as we are aware only one of them (viz. Tumlirz on Potential) has been translated into English; but it would well repay any one who can spare the time to make translations of some of the other volumes, and certainly of the one before us.

The problem of the measurement of electricity for commercial and domestic purposes is one which so far has only been very unsatisfactorily and incompletely solved, although the demand for

a really workable and reliable electricity meter is already great and daily increases. The author endeavours in this little hand-book to give a clear idea of the principles and details of construction and action of the various forms of meter for quantity, power, and energy, which are or have been in practical use both here and abroad. The figures are extremely well executed and help largely to a clear understanding of the apparatus. At the end of the book will be found a summary of the conditions under which electrical energy is supplied in various cities, and the charges which are made for it. Indeed no pains have been spared to make the volume as handy and yet as complete as possible, and we would again urge the desirability of its translation into English. J. L. H.

LXVI. *Intelligence and Miscellaneous Articles.*

To the Editors of the Philosophical Magazine and Journal.

NOTE ON THE ELECTRICAL CONDUCTIVITY OF HOT GASES.

GENTLEMEN, Cambridge, May 14, 1891.

IN reference to Dr. Arrhenius' remarks in the paper with the above title in the last number of the 'Philosophical Magazine.' I have to observe :—

1. With regard to the question as to the action of an excess of hydrogen on the dissociation of HI, HBr, or HCl : though Dr. Arrhenius says that such an excess *need* not diminish the dissociation, the question is not really an open one, as Lemoine's experiments (*C. R.* lxxxv. pp. 34–37) have proved that as a matter of fact an excess of hydrogen produces a large diminution in the dissociation of HI.

2. Dr. Arrhenius attributes the conductivities of the hot HCl, HBr, HI, which I observed to the production of platinum dust by the action of the halogens on the platinum of the vessel in which the gases were contained, and also upon the electrodes. As, however, the experiments were made in earthenware as well as in platinum vessels, and with carbon, gold, and iron electrodes as well as platinum ones, this explanation is quite inadmissible. Again, not only the halogens, but also the vapours of most metals conduct when hot, and this whether surrounded by nitrogen or air. In my experiments the effect of surrounding the gas by nitrogen instead of air was always tried.

3. With reference to Crafts's experiments on the dissociation of the halogens, I may observe that a trace of dissociation would produce a much greater effect on the conductivity than on the vapour-density, and that the temperature vaguely described as yellow heat extends over a wide range, and two temperatures, each of which might by different observers be described as yellow heat, might easily differ by several hundred degrees Centigrade.

I remain, Gentlemen,

Your obedient servant,

J. J. THOMSON.

PROPAGATION OF HERTZ'S OSCILLATIONS IN AIR.
BY MM. E. SARASIN AND L. DE LA RIVE.

We have had the honour of presenting to the Academy the first results which we obtained in repeating the beautiful experiments of M. Hertz on rapid electrical oscillations (*Comptes Rendus*, Jan. 13, 1890). We there limited ourselves to the case in which the electrical oscillation is transmitted along a conducting wire. We have since then repeated another of M. Hertz's experiments, which consists in following the propagation of electrical induction through air in the absence of any metallic conductor. The primary exciter is placed in front of, and parallel to, a large plane metal surface; the electrical oscillations which proceed from it, travelling through air, reach the metal surface, which acts as a mirror; the reflected waves form then, with the direct waves, a system of stationary waves, the first node of which is at the mirror.

In order to examine the system of vibrations which are set up in front of the mirror, the circular resonator is moved about in two different principal positions: first, keeping it always parallel to the mirror and to the primary, that is, in the plane of the wave; secondly, moving it in the plane perpendicular to the mirror through the axis of the primary—the plane of vibration. In both cases the results are absolutely concordant as to the position of the equidistant maxima and minima of electromotive force. Besides these two methods Hertz employed a third, which consists in producing interferences on the same resonator between waves arriving from the same exciter, either directly across the air or by a conducting wire. From these experiments he concludes, by the great wave-lengths from the mirror, that the velocity of propagation through air in the absence of any conducting wire is almost twice as great as that which is observed along a wire; that the two velocities are to each other as about 7 to 4, in opposition to the theory of Maxwell, according to which these velocities should be equal.

From its theoretical importance, we have especially applied ourselves to the verification of this particular point. Having observed, from our previous experiments along wires, the constancy of the undulating period of a given circular resonator whatever be the primary exciter by which it is set to work,—the same exciter, in short, permitting the observation of as many wave-lengths as there are circles of different magnitudes—we have devoted ourselves to comparing the wave-length given by the same circular resonator along wires with those which it gives in air without wires.

We used as a reflecting surface a large curtain of sheet lead, 2·5 metres in height by 3 metres in breadth, kept plane and vertical by its own weight. The primary exciters and the large Ruhmkorff's induction-coil were the same as those which we used in our preceding researches. The exciter was placed in front of the mirror, with its axis horizontal, and its break on the perpendicular to the centre of the metal sheet; its distance was between 4 and 10 metres. The circular resonator was fixed on a sliding chariot along a large wooden optical bench.

We have greatly varied the conditions of the experiment, and repeated the observations a great number of times.

We collate in this Table the results we have obtained with five different circles*.

Diameter of the circle D.	1 m. stout wire 1 cm. *d.*	0·75 stout wire.	0·50 stout wire.	0·35 stout wire.	0·35 fine wire, 2 mm. *d.*	0·25 stout wire.	0·25 fine wire.	0·20 stout wire.	0·20 fine wire.	0·10 stout wire.
1st Loop.....	2·11	1·60	1·11	0·76	0·75	0·46	0·54	0·39	0·42	0·21
1st Node... ..	4·14	3·01	,,	1·49	1·51	0·94	1·17	0·80	0·93	0·41
2nd Loop ...	,,	,,	,,	2·30	2·37	1·63	1·89	1·24	1·55	0·59
2nd Node ...	,,	,,	,,	3·04	3·10	2·15	2·40	1·69	2·05	0·79
3rd Loop ...	,,	,,	,,	,,	,,	2·71	2·91	,,	2·46	0·96
3rd Node ...	,,	,,	,,	,,	,,	3 14?	,,	,,	,,	,,
½ λ Air	2·03	1·41	1·11	0·76	0·80	,,	0·60	0·43	0·51	0·19
½ λ Wire ...	1·92	1·48	0·98	0·73	,,	,,	0·56	,,	0·45	,,
2 D	2·00	1·50	1·00	0·70	0·70	,,	0·50	0·40	0·40	0·20

We give in this Table the means of the measurements obtained with each circle, and for the sake of brevity we have not separated those made with primary exciters of different dimensions, as these did not present systematic differences. In these latter experiments in air, as in our previous researches along wires, we have in part established that *a circular resonator always gives the same wave-length*, even when the dimensions of the primary are varied within certain limits†. Then, again, is observed what we have called multiple resonance.

In the case of larger wave-length circles of 1 m. and of 0·75, we can scarcely determine with any precision more than a node and a loop, besides the node on the mirror itself. With smaller circles for which the dimensions of the mirrors are somewhat more suited we can easily determine three loops and three nodes, including that of the mirror. The equidistance of the loops and nodes is, as will be seen, pretty satisfactory ‡.

The most important result of our research follows from the comparison of the figures of the three last lines of the Table, which show that the wave-length obtained for each circle in the case of

* The delicacy of the micrometric screw is a very important element in this kind of research, especially with the small circles, which only give very feeble sparks. In the latter case we used a screw giving the $\frac{1}{10}$ of a millim.

† As the intensity of the spark of the resonator is feebler in this experiment than in that of the wires, and as it diminishes, moreover, much more rapidly as we move away from the primary, the observation is altogether less precise than with wires. In order to work in good conditions the primary should have dimensions suited to the diameter of the resonator. The limits within which we can conveniently observe multiple resonance are less extended than in the case of wires, but vary up to double or even more.

‡ M. Hertz places the first node at a certain distance behind the mirror; this perturbation at the end does not seem to follow from our experiments. As will be seen from the Table, the first quarter of a wave-length presents no systematic difference from the others.

propagation through air is very sensibly equal to that which this same circle gives along wires, the quarter of each being itself almost equal to twice the diameter of the corresponding circle. From this it follows that *the velocity of propagation of Hertz's electrical oscillations across air is very nearly the same as that with which they are transmitted along a conducting wire**.—*Comptes Rendus*, March 31, 1891.

ON AN IMPROVED METHOD OF DETERMINING SPECIFIC HEATS BY THE ELECTRICAL CURRENT. BY PROF. J. PFAUNDLER.

The method published by the author in 1869, which depends on Joule's law, in which one and the same current develops quantities of heat, in coils of wire arranged in series, which are proportional to the resistances, has hitherto found but few applications from the circumstance that it only applies to non-conducting liquids. The author has got rid of this drawback by substituting for the coils of wire spiral glass tubes filled with mercury. He has also given the method far greater accuracy and certainty by inserting three mercury resistances in the branches of a Wheatstone bridge, by which it is possible to control and keep constant the ratio of the resistances during the passage of the heating-current. Small variations in resistance are compensated by introducing glass threads in the straight ends of the tubes which contained the mercury. In other cases these changes are measured by displacing the contact-key, and in this way the result is corrected.

The comparative measurement of the rise of temperature is made more delicate by means of a thermopile.

As instances of the utility of the method, experiments were made both with continuous and with alternating currents. The attempts of the author to use this method for the determination of the thermal capacity of water at different temperatures were interrupted by the author's transference to Grätz, and will be repeated on a larger scale; these experiments are to be regarded as preliminary ones intended to test the method.—*Wiener Berichte*, April 9, 1891.

ON PERIODICALLY VARIABLE ELECTROMOTIVE FORCES WHICH ACT ONLY IN ONE DIRECTION IN A CONDUCTOR WITH SELF-INDUCTION. BY PROF. PULUJ OF PRAG.

In this paper the laws of the flow of electricity in a conductor with self-induction are theoretically investigated, when the external

* We have already enunciated this in a preliminary communication made on this subject to the Société de Physique et d'Histoire naturelle de Genève at a meeting on May 1, 1890 (*Archives des Sciences phys. et nat.* vol. xxiii. p. 557); we have since then completely repeated the researches by varying the conditions in a number of ways, and it is this latter research which we give here. M. Lecher, in Vienna, has found by an entirely new method that the velocity of electrical undulations along a wire is equal to that of light.

electromotive force is a quadratic sine-function of the time, and impulses are produced in the conductor in only one direction. Calculation gives the result, that while the electromotive force varies between zero and a maximum value, the momentary current-strength is always different from zero, and varies periodically between a minimum and a maximum value. The mean current-strength is independent of the self-induction and has always the same value, whether the self-induction of the conductor is very large or is equal to zero. The self-induction causes no loss of mean current-strength; its action only consists in making the waves plane. Formulæ are given for the mean square of the current-strength, and for the work developed in the circuit, from which formulæ it can be seen that the magnitudes adduced depend on the displacement of phase, and satisfy the law of the superposition of the actions of two components of electromotive force. In conclusion the analogy is pointed out which exists between the laws investigated of electrical flow and those of the rotatory motion of a heavy wheel under the action of successive mechanical impulses.— *Wiener Berichte*, April 23, 1891.

ON WHEATSTONE'S DETERMINATION OF THE VELOCITY OF ELECTRICITY. BY PROF. J. STEFAN.

In the paper on the Motion of Electricity in Wires, Kirchhoff in 1857 first showed that in certain conditions electricity moves in a thin wire according to the laws of wave-motion, and with a velocity which can be put equal to that of light. The agreement between the velocities of electricity and of light only holds, however, when electricity travels in a straight wire stretched in the air. Kirchhoff restricted his investigation to this case. If we apply the bases of his calculation to other cases, for instance, a wire which is bent backwards and forwards in zigzag or is wound in a spiral, it is found that electricity travels under these conditions with a far greater velocity.

In Wheatstone's well-known method twenty plane windings of drawn-out wire were used, and the velocity of electricity was found by this measurement to be half as much again as that of light. In the preceding I think I have given the correct explanation of this result. I have, however, also attempted to give this explanation an experimental basis, and for this purpose I have employed the method given by Hertz of producing stationary electrical waves in wires. I have used a similar conductor to that of Wheatstone, but on a smaller scale, and connected it with a couple of long straight wires, and compared the length of a wave in the conductor with the length of the same wave in the straight wires. The wave in the conductor is considerably longer, and in accordance with this the velocity of electricity in the conductors is greater than in the straight wires, and, according to my experiments, in a ratio which still exceeds that found by Wheatstone.— *Wiener Berichte*, April 23, 1891.

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